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An Investigation of the Recovery of Volatiles from Waterberg Coal

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Abstract

South Africa has large coal reserves in world terms and the coal mining industry serves an important role in supporting the South African economy. Currently, most of the coal is mined in Witbank and Highveld Coalfields, where it occurs in relatively thick seams, near the surface. However, these coalfields are fast becoming depleted and new techniques are required to utilise the large coal resources still available in South Africa, especially in the Waterberg region, where a significant number of low-grade seams may be mined but discarded.

The Waterberg region contains approximately 40% of the remaining coal in South Africa. However, the lithology of most of the coal seams is such that separation of the gangue minerals by density is difficult. There are many problems associated with mining in the Waterberg region, which include lack of infrastructure, lack of water sources, environmental issues (groundwater pollution) and socio-economic issues (Jeffrey, 2005).

The experimental part of the project was aimed at investigating the recovery of chemicals from Waterberg coal which has a high mineral content. The design and simulation part of the project utilised the data obtained from laboratory experiments, to determine if a reactor with counter-current flow of gas and solids could be used to recover the volatile material from the coal. It was envisaged that the volatile material would be removed in the upper zone of the reactor, by hot gas generated by combustion of char in the lower zone. It was also envisaged that the air for combustion would be pre-heated, using heat exchange with the exit gas, as practiced in power stations. A mass and energy balance calculation was done over the entire system, to determine the limits of mineral content (expressed as ash content). Since, a large quantity of energy is required to raise the temperature to the point where volatiles can be separated, particularly if there is a high mineral content, the proportion of char is important, to provide sufficient energy to drive the process. It was envisaged that heat exchange would conserve energy and that it may be possible to use coal containing a relatively high mineral content, which would normally be discarded.

Laboratory experiments were conducted on single coal pieces, which were first subjected to pyrolysis in a horizontal tube, which was inserted into a muffle furnace. A stream of nitrogen was used to transport the volatile material to an external collection vial, submerged in an ice bath. Some of the volatile material condensed in the cooler portions of the reactor, but it was recovered by subsequent dissolution in a solvent. The remaining char was then heated in a furnace with air, to burn the carbon and to determine the mass of ash remaining. The temperature and time for pyrolysis and combustion were varied, to determine suitable

operating conditions. The liquid products were analysed using the Karl Fischer method and GCMS analysis

Four series of experiments were conducted, having a different variables changed. The first variable that was investigated, was the size of the coal sample. Single coal particles, with varying mineral content, were used. The mass of the coal piece was about 40g and the dimensions were about 50mm x 25mm x 30mm) The combustion experiments showed that these particles were not fully combusted, as they had an unreacted core. The subsequent series of experiments were conducted on single particles with a mass in the range 7g to 23g.

The pyrolysis experiments show that significant amounts of the liquid product condensed inside the reactor tube. The combustion experiments showed that the structure of the high ash samples was maintained, whilst the low ash samples disintegrated. This is an important factor as the coal dust would cause channelling of the gas flowing up the reactor.

The second variable that was investigated was the effect of time. The results showed that 30 minutes was sufficient to extract the hydrocarbons. It was noted that the coal with a high mineral content (> 60% ash) contained a relatively large amount of volatiles (17 %), and very little water (< 2 %). The GCMS analysis showed the presence of large proportion of phenols. Phenols are an important commodity and have a wide range of industrial applications. Karl Fischer analysis revealed that the overall water content was low and this made the liquid product easier to upgrade.

The experimental results were then utilised in a mass and energy balance calculation, to simulate the proposed counter-current reactor and external heat exchangers. Two scenarios were investigated; The first was with the pyrolysis temperature set at 600°C and the combustion zone set at 800°C. The data from samples with varying mineral content was analysed. (The ash content of the feed ranged from 25.7% to 65.8%). The amount of excess energy available reduced as the mineral content increased, but the process still worked when the ash content of the combusted material reached 65.8%. The second scenario was with worst coal (65.8% ash), the pyrolysis temperature set to 700°C, and the combustion temperature set at 950°C. The results showed that there was still sufficient energy released by the combustion of the char to operate the process, but there was a smaller excess of energy. Additional water was needed to reduce the temperature of the product stream (hydrocarbons).
It should be noted that loss of energy from the high temperature zones by conduction was not considered and that some of the ‘excess energy’ will be needed.

Declaration

The work presented in this dissertation was carried out in the Thermodynamic Research Unit in the School of Chemical Engineering at the University of KwaZulu-Natal, Durban, from January 2013 to December 2016 under the supervision of Professor B.K.Loveday and Professor D.Ramjugernath.

This dissertation is submitted as the full requirement for the degree M.Sc (Eng) in Chemical Engineering.

I, Varnika Govender, therefore declare that:

(i) The research reported in this dissertation, except where otherwise indicated, is my original work.

(ii) This dissertation has not been submitted for any degree or examination at any other university.

(iii) This dissertation does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.

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(a) Their words have been re-written but the general information attributed to them has been referenced;

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(v) This dissertation does not contain text, graphics or tables copied and pasted from the internet, unless specifically acknowledge, and the source being detailed in the dissertation and in the References sections.

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Varnika Govender

As the candidate's supervisor, I, Professor B.K.Loveday, approved this dissertation for submission.

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Professor B.K.Loveday

As the candidate's co-supervisor, I, Professor D.Ramjugernath, approved this dissertation for submission.

_____
Professor D.Ramjugernath

Dedication

To My Parents

Kumeras Thandrayen & Shobana Govender

Thank you for your patience, understanding, unconditional love and support. This was only possible with your blessings and good wishes.
Love you both always.

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Table of Contents

List of Figures

List of Tables

Chapter 1

Introduction

The rising demand for electricity has depleted South Africa's coal stocks that are mainly obtained from the Highveld and Witbank coalfields. This has made it necessary to find alternative sources of coal to meet current and future demands.

The Waterberg coalfields have emerged as an important source of coal. This coalfield contains significant resources, making up approximately 40% or 75 billion tonnes (Theunissen, 2012) of South Africa's remaining reserves. However, there are many problems associated with mining these coalfields. Some of the major problems include the complex geology of the coalfields (coal extraction and beneficiation is difficult), lack of proper infrastructure (due to the remote location of the mine all necessary equipment and supplies would have to be brought in), lack of water sources, environmental impact (potential groundwater pollution), as well as socio-economic issues (lack of skilled labour in the area) (Jeffrey, 2005). Significantly, as a result of the geology, most of the coal is low grade since it is intercalated with mudstone (Theunissen, 2012), however, the coal quality is high. Beneficiation by traditional methods is costly and it appears that a significant amount of potentially valuable material is discarded.

Since there are many drawbacks to mining the Waterberg coalfields, and in order to make its exploitation viable, it is necessary to utilize the mined coal effectively, by reducing wastage and the loss of potentially valuable material. In addition, avenues for generating income must be identified. To this end, ways in which value can be obtained from high ash coal from the Waterberg Coalfields should be explored.

The ash content of thermal coal provided to Eskom must not exceed 35% (Steyn and Minnitt, 2010), which implies that majority of the coal is discarded if it does not meet the specifications. It is imperative to make effective use of this coal. Additional coal can be obtained at very low cost, by collecting some coal seams which are currently discarded during open-pit mining. Coal from the Waterberg usually requires 'washing' in a heavy medium plant, to achieve this quality of product. The discard from this process could be upgraded to a coal with an ash content of about 50%, using an additional washing stage. It is known that Waterberg coal has a relatively high proportion of volatile material and recovery of volatiles from high-ash Waterberg coal.

If the volatile material occurs in significant quantities and produces saleable products, extraction of the Waterberg coal would be financially lucrative. The generation of a staged coal conversion process which enables the production of energy to drive the process alleviates extra costs.

The subject of this investigation is the recovery of volatile material from high ash Waterberg coal. The remaining char is combusted to provide the energy for pyrolysis and counter-current heat exchange is essential to achieve this end.

The project consisted of two parts, namely the experimental portion and the design portion. In the experimental part the coal samples were subjected to pyrolysis, followed by combustion. The coal samples were classified according to ash content. For the purposes of this dissertation ash refers to the non-combustible residue remaining after combustion. Coal pieces, (about 20 x 30 x 50 mm) were first subjected to pyrolysis in a furnace, using a stream of nitrogen to drive off the volatiles. Some material condensed in the cooler portions of the reactor, but were recovered by dissolution in a solvent. The remaining char was then heated in a furnace with air, to burn the carbon and determine the mass of ash remaining. The structure of the remaining ash was noted.

The hydrocarbon samples were subjected to GCMS analysis, which identified the compounds and provided an indication of the amounts present in the sample. A Karl Fisher titration was used to measure the amount of water present. It is envisaged that the liquid product obtained from the proposed process will be separated into various fractions by distillation (i.e. separated according to relative volatility).

The combustion part of the experimental section provided the ash content of each sample. The samples with moderate ash content (25% - 35%) disintegrated into powder when combusted. However, the samples with a high ash content retained the original structure. They were therefore more suitable for the proposed process, which requires counter current flow of gas and solids.

Coal with a high ash content, which is currently discarded, may oxidise and cause water pollution (acid mine drainage). The process envisaged will burn the char and the remaining ash may be less damaging to the environment.

There are many commercially available processes for extraction of the volatile portion of coal, using pyrolysis, such as the Char Oil Energy Development process, the TOSCOAL process, the Lurgi-Ruhrgas process, the Occidental Flash process, and the Clean Coke process (Lee, Speight and Loyalka, 2015).

The second part of the project involved the design of a mass and energy balance circuit which utilised the data from the experimental work. The total energy required for recovering the chemicals was calculated, and a counter-current moving bed was simulated, using an EXCEL spreadsheet, for effective heat exchange between solids and gas. Heat exchange with the incoming air was also used to condense the volatile components and preheat the air prior to combustion. The operating limits of the process were investigated, particularly the ash content of the coal. Start-up and temperature control were also considered. Heat losses were not taken into account as it is dependent on the size of the equipment.

Figure 1.1: High ash content coal sample obtained from the Waterberg Coalfields (> 45 % ash content)

Chapter 2

Literature Review

2.1 Introduction to the Global Coal Industry

Coal is one of the most important sources of energy in the world. Since it is an abundant commodity, it serves as an affordable source of energy. The primary use of coal worldwide is in the production of electricity. Other uses include serving as a reductant in the steel manufacturing industry and coal provides the energy required in cement production. Coal is utilised to produce 70% (BASIC COAL FACTS, 2017) of the world's steel. Coal accounts for approximately 41% (BASIC COAL FACTS, 2017) of the world's total electricity production and 29% (Coal, 2017) of the world's energy supply.

Approximately, 90% of coal exports are derived from the following six countries namely; Indonesia, Australia, Russia, Colombia and the United States of America (Coal, 2017). Coal has been the fastest growing resource since the beginning of the 21st century and the global supply is expected to increase steadily by 0.6% (Coal, 2017) up to 2020. Export of steam coal, coking coal and lignite increased by 1.9% (Coal information: Overview, 2017) whilst the global coal consumption decreased by 1.9% (Coal information: Overview, 2017).

The conversion of conventional motor cars to electric cars, will increase the demand for electricity. This is may result in the increase in the use of coal for power stations.

2.2 South African Coal Industry

South Africa has one of the world's largest coal reserves, approximately 3.5% ("Coal - Chamber of Mines South Africa", 2017), and the coal mining industry serves an important role in boosting the South African economy. South Africa has a production rate which constitutes 3.3% ("Coal - Chamber of Mines South Africa", 2017) of the world's annual production. It has the sixth largest coal reserves, and it is the sixth largest coal exporting country in the world, exporting 6% ("Coal - Chamber of Mines South Africa", 2017) of coal globally.

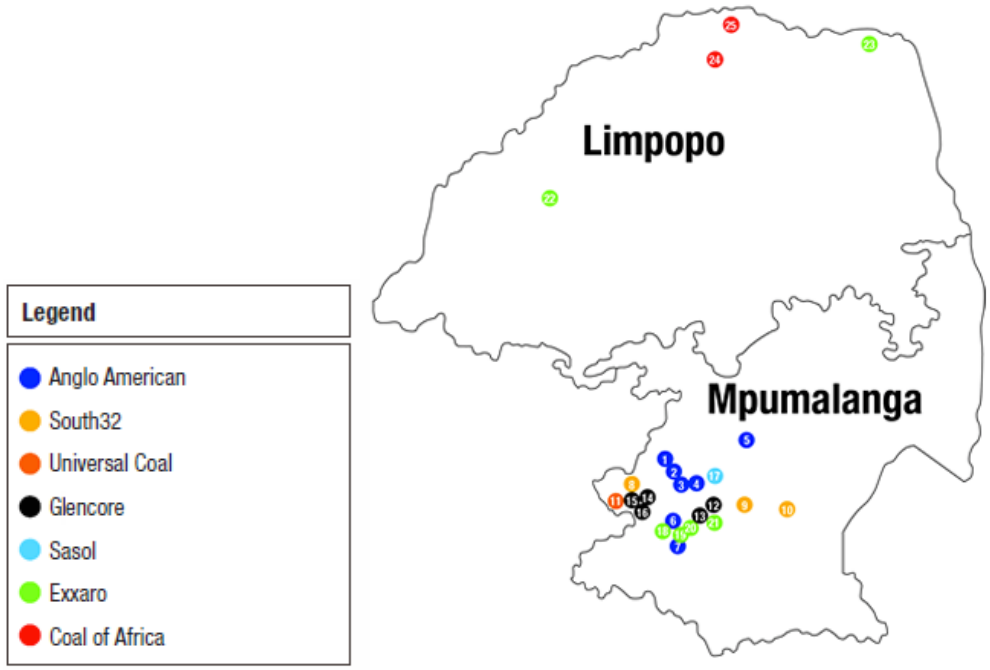


Figure 2.1: Depicting Active Coal Mines found in South Africa ("Coal - Chamber of Mines South Africa", 2017)

South African coal currently provides around 81% ("Coal - Chamber of Mines South Africa", 2017) of the country's electricity requirements as supplied by Eskom. Coal is preferred as it is abundant and it is a relatively cheap source from which electricity can be produced. Currently, there are 25 coalfields, owned by various companies, from which coal is mined as seen in Figure 2.1. The Waterberg coalfield, which is in the north west of Limpopo, is currently mined by Exxaro. The Waterberg, Witbank and Highveld coalfields contain the highest concentration of coal in South Africa amounting to 70% of the country's total reserves (Jeffrey, 2005).

Coal is mostly sourced from the Witbank and Highveld coalfields since, due the geological structure of the coalfields, it is financially viable. But, these coalfields are fast becoming depleted, and new coalfields need to be opened. The Waterberg coalfield has been identified as the most attractive source for expanding coal production, but some of the seams are difficult to upgrade. New techniques are needed to extract, and effectively utilize, this coal resource.

2.2.1 Coal beneficiation and export of low-ash coal

Run-of-mine coal is usually upgraded using heavy-medium separation. The low ash product (approximately 10% ash) is transported to Richards Bay via a dedicated railway line and exported. The selling price of export coal has been double the price than that obtained for thermal coal delivered to Eskom. The price obtained for exported coal increased when the price of oil increased, and this led to an increase in the rate of coal export from South Africa, sometimes with an ash content up to 14%. This led to a reduced supply for Eskom. The recent fall in the price of oil has led to a fall in the price of export coal (Mathews, 2017). China and India are the largest global importers of coal hence the demand for coal is controlled by these countries (Mathews, 2017).

2.3 Coal

Coal is defined as a combustible sedimentary rock formed by the accumulation of plant matter, which has been transformed by physical, chemical, and biological processes (Singh, 1997). Coalification (formation of coal), is affected by the following factors: Climatic conditions (humid and damp areas), time (older samples have a higher rank), depth of burial (the ratio of fixed carbon to volatiles increases) and orogenic activity (increased activity increases coal rank) (Singh, 1997).

2.3.1 Types of Coal

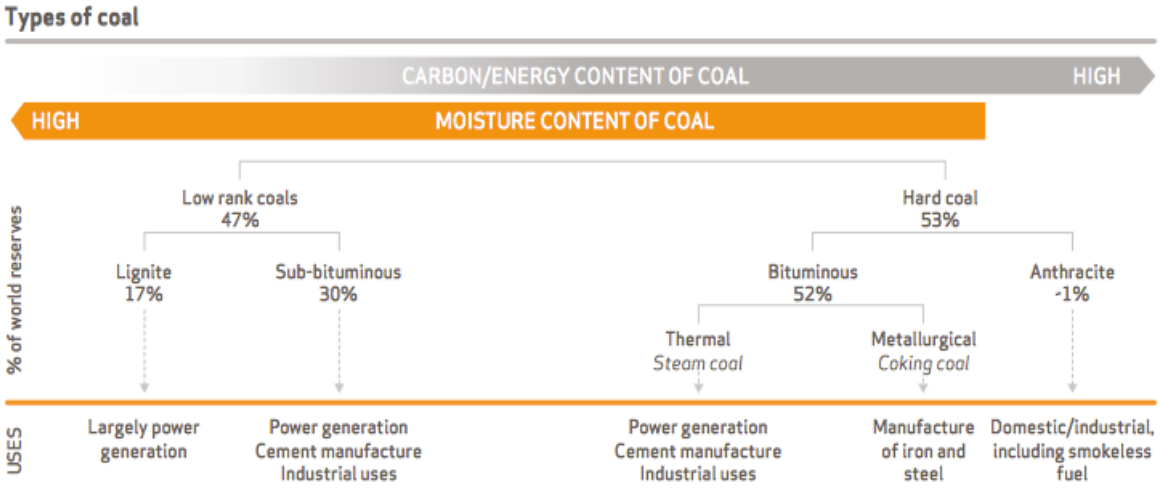


Figure 2.2: Coal Rank and Type (BASIC COAL FACTS, 2017)

Coal is ranked from lowest to highest quality in the following order: peat, lignite, bituminous, and anthracite coal. The different ranks of coal have different characteristics. Peat is ultimately converted into anthracite under conditions of temperature, pressure and time. Peat usually occurs as unconsolidated soft material at the top of a coal bed, has a very high moisture content, and varies in colour from brown to black.

Lignite occurs at relatively shallow depths in unconsolidated sands and clay. The coal is yellowish to dark brown in colour and has a dull appearance (Singh, 1997). It has relatively high moisture content between 25% - 50% and a carbon content between 60% - 70% (Riazi and Gupta, 2016) on a dry ash free basis.

The next main category of coal is Bituminous Coal, which is a high-ranking coal, harder and darker in colour than lignite. This coal also has a high carbon content.

Figure 2.3: Bituminous Coal Sample (Bowen & Irwin, 2008)

Anthracite is the most mature coal, having the highest carbon and energy content. According to Figure 2.2, it makes up approximately 1% of world reserves. The moisture content is low, and it has a shiny appearance. Anthracite has a carbon content over 87 % (Riazi and Gupta, 2016) on dry ash-free basis. It can be further divided into semi-anthracite, anthracite and meta-anthracite based on the carbon content (Riazi and Gupta, 2016).

2.4 Waterberg Coalfield

In view of the size and importance of the Waterberg Coalfield, more details of this resource are given below:

The Waterberg coalfield is situated about 400 km North-West of Johannesburg in the Limpopo province. It is listed as the fourth largest reserve in the world and it contains approximately 75 billion tonnes of coal, currently about 40% of South Africa's total coal reserves (Theunissen, 2012).

The Zoetfontein Fault in the north and the Eenzaamheid Fault in the south form the boundaries of the Waterberg basin ("Kumba Resources - Independent Competent Persons Report on Exxaro Resources: Geology", 2013). The faults form a boundary spanning 88km from east to west and 40km from north to south ("Waterberg Coal Project – The Waterberg Coal Company Ltd", 2015). The Zoetfontein, Eenzaamheid and the Daarby faults function to create and maintain the characteristics of the coal.

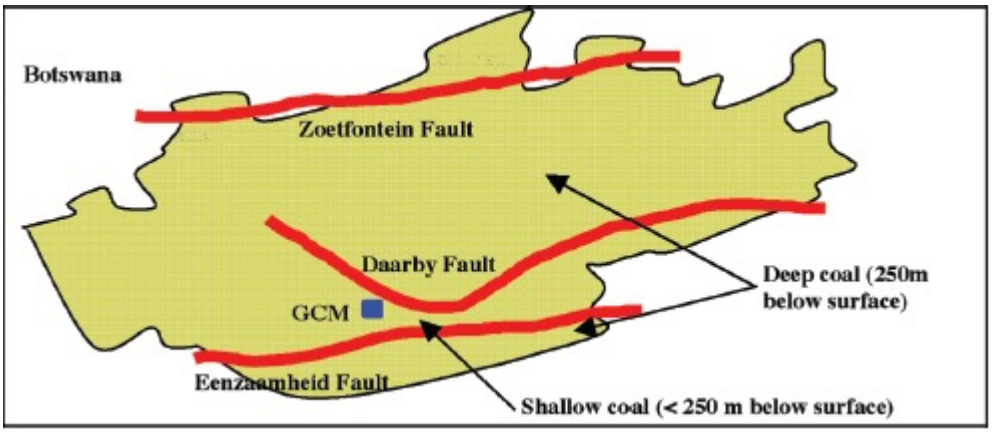


Figure 2.4: Waterberg Basin bound by the Zoetfontein and Eenzaamheid Faults (Jeffrey, 2005)

Figure 2.4 illustrates the major formations found within the Waterberg basin, which are separated by faults. The information provided by Exxaro states that the lower Ecca group found towards the south of the Waterberg basin has very limited differences in the lithology indicating a very slow rate of subsidence.

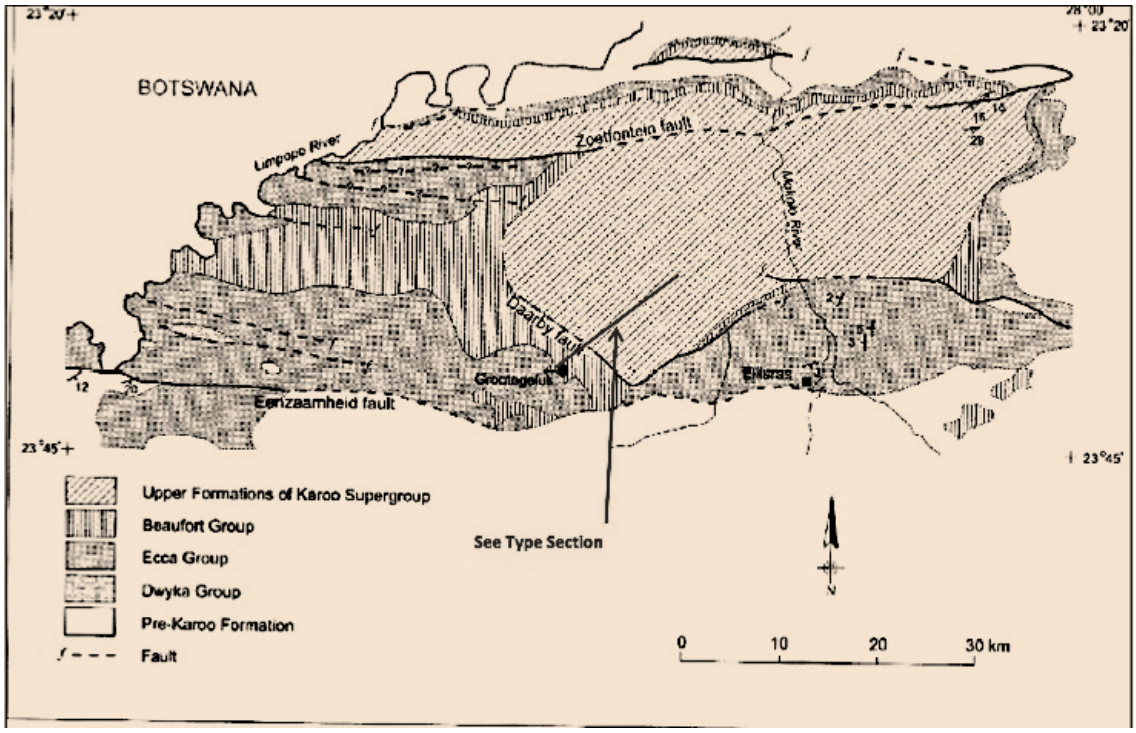


Figure 2.5: Geology of the Waterberg Basin (van Wyk & Barker, 2013)

2.4.1 The Ecca Group

The Ecca Group is found towards the southern part of the Waterberg basin. The main coal bearing seams of the Ecca Group are the Volksrust formation, consisting of a 55m seam of intercalated mudstones and coal, and the Vryheid formation, made up three major seams of 3m, 9m and 4m in width ("Kumba Resources - Independent Competent Persons Report on Exxaro Resources: Geology", 2013).

The Volksrust formation differs lithologically from the Karoo Basin. The Volksrust formation has coal intercalated with carbonaceous shale. The upper zones have semi-soft coking coal with a high vitrinite content whilst the lower sections contain low grade thermal coal for use in power stations ("Kumba Resources - Independent Competent Persons Report on Exxaro Resources: Geology", 2013). The Vryheid formation also contains coal intercalated with mudstone yielding coal suitable for use in power stations. The Volksrust Formation coals are classified as a thick interbedded seam deposit type and the Vryheid Formation as a multiple-seam deposit type.

2.4.2 Problems Associated with Mining the Waterberg Basin

2.4.2.1 Market for the Coal

A large proportion of the Waterberg deposit is low-grade, having a large mineral content. This type of coal is not suitable for mining at depth and it is difficult to upgrade using existing processes. The estimated mass of saleable coal would be only 50% of the mass of coal mined and this could rule out underground mining of some seams (Jeffrey, 2005).

2.4.2.2 Extraction

Preliminary geological mapping has indicated that the Waterberg coalfields are of a complex nature. Figure 2.5, indicates the major fault lines found within the Waterberg coalfield, which provide an indication of areas having similar stratigraphy. Since detailed geological mapping is unavailable, positions of minor fault lines are unknown hence jeopardizing potential mining in the area.

Approximately, 75 % of the coal is found within deep coal seams ranging from 250m – 400m (Jeffrey, 2005). Increased depths correspond to increased costs in extracting the coal.

2.4.2.3 Beneficiation

Coal found in the Waterberg is intercalated with shale and mudstone thereby making separation difficult and costly. Liberation of coal by comminution from the gangue is important to yield a viable product. It is also one the most expensive components of the mining process. Large quantities of waste are generated since much of the coal does not meet standards for export or use in existing processes (Jeffrey, 2005).

2.4.2.4 Water

Large volumes of water are required to conduct the essential mining processes (such as separation). However, the Waterberg doesn't have sufficient surface or ground water sources. Water needs to be piped in from surrounding dams or rivers, thereby increasing operational costs (Jeffrey, 2005).

It is concluded that other processes for extracting value from the coal need to be considered, such as chemical extraction, to ensure that the true value of the Waterberg coal field can be realised.

2.5 Coal Liquefaction

Coal liquefaction is defined as a process wherein the aim is to produce a liquid product with an increased hydrogen-to-carbon ratio, a reduced amount of heteroatoms (sulphur, nitrogen and oxygen) and a minimal inorganic content (Kent, 2010).

Coal liquefaction can be achieved in three ways, namely:

- Direct liquefaction
- Indirect liquefaction
- Pyrolysis

2.5.1 Direct Liquefaction

Direct liquefaction is also known as hyrdroliquefaction, since the process is carried out in a hydrogen filled environment (Lee et al., 2015). The process can include one or two stages. In the two-stage processes, a 'liquid product' is formed first and in the second stage, a vapour phase hydrogenation is used to produce light fuels by catalytic conversion (Lee, 1996). There are many commercial processes such as H-Coal, Solvent Refined Coal (SRC-I, SRC -II) and Exxon Donor Solvent.

One of the oldest processes is the Bergius-IG Hydroliquefaction process, which was developed in Germany. This two stage process is no longer commercially used due to the extreme operating conditions. Coal was catalytically converted in the presence of hydrogen and an iron oxide catalyst at 450°C - 500°C and 200 – 690 bars (Lee et al., 2015) with a residence time of 80-85 minutes. Light oil, 'middle' distillates, and a residuum were produced.

2.5.2 Indirect Liquefaction

Indirect liquefaction is defined as a process wherein the coal reacts with oxygen and steam at a high temperature to produce a synthesis gas. The overall reaction with carbon may be summarised as follows:

$$2C + H_2O + O_2 \rightarrow CO + H_2 + CO_2 \qquad (2.1)$$

The synthesis gas, which contains carbon monoxide and hydrogen, is catalytically converted to liquid products (Jinsheng, 2009).

There are two well-known processes, namely:

- Fischer-Tropsch Synthesis
- Methanol Synthesis

In the Fischer-Tropsch process, synthesis gas is catalytically converted to primary products or wax, a hydrogen carbon condensate, a tail gas, and reaction water (FISCHER-TROPSCH SYNTHESIS, 2017). Figure 2.6 is a simplified block diagram, which illustrates how the Fischer-Tropsch process is used to produce hydrocarbon products.

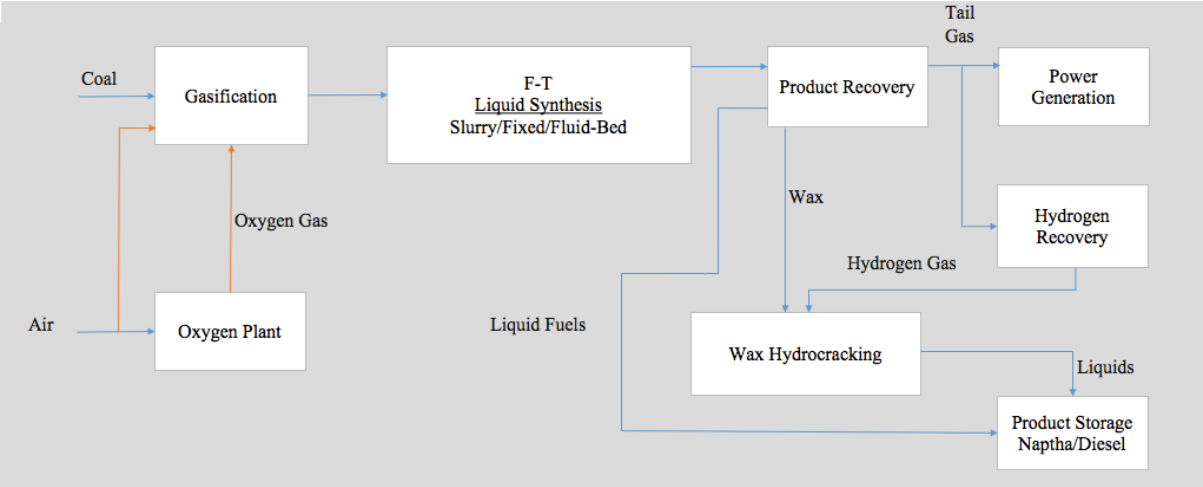


Figure 2.6: Indirect liquefaction using Fischer-Tropsch Conversion (FISCHER-TROPSCH SYNTHESIS, 2017).

The Fischer-Tropsch process converts the carbon monoxide (CO) and hydrogen from the synthesis gas into hydrocarbons by the following generalized chemical reaction (FISCHER-TROPSCH SYNTHESIS, 2017):

$$(2n+1)\ H_2 + n\ CO \rightarrow C_nH_{(2n+1)} + n\ H_2O \qquad (2.2)$$

The catalysts used in the process are either iron or cobalt based and also control the final composition of the product stream (FISCHER-TROPSCH SYNTHESIS, 2017).

It is important to note that the production of synthesis gas requires a stoichiometric amount of water, and this amount of water this is not available in the Waterberg area.

2.5.3 Coal Pyrolysis

Pyrolysis is defined as the thermochemical decomposition of coal at elevated temperatures in the absence of oxygen (Speight, 2012). Coal pyrolysis is a fairly complex process involving a large number of chemical reactions to yield condensable tar, oil, water vapour, non-condensable gas and solid char (Lee et al., 2015). Pyrolysis yields products via a process known as destructive distillation (Lee et al., 2015). The process of destructive distillation results in fragmentation of the C-C bonds in macromolecular structure of the coal particle. These reactions enable the conversion of solid fuel into liquid and gas fuel products.

Pyrolysis can be divided into four categories namely slow pyrolysis, conventional pyrolysis, fast pyrolysis and flash pyrolysis. The methods are characterised according to their operating conditions, which directly affects the yield and types of products formed. A summary of the major operating conditions is given in Table 2.1 (Peacocke & Joseph, n.d.).

The slow and conventional pyrolysis processes have very similar operating conditions, which are low reactor temperatures, long solid and vapour residence time and slow heating rates (Peacocke & Joseph, n.d.). These processes are differentiated from each other by the overall product composition. Slow pyrolysis yields equal proportions of char, tar and gas by mass (Peacocke & Joseph, n.d.). In the conventional pyrolysis process yields are mainly based on the composition of the feedstock, however the organic liquid yield is much lower, whilst char, water and non-condensable gases make up the remainder of the product composition in unequal proportions (Peacocke & Joseph, n.d.).

Flash pyrolysis and fast pyrolysis process can be differentiated from each other due to their operating conditions. Flash pyrolysis operates under moderate conditions whilst fast pyrolysis operates at higher temperature, at a faster heating rate and has a very short vapour product retention time as seen in Table 2.1. Fast pyrolysis is favoured when liquid and gaseous product yield should be maximized.

Table 2.1: Main operating conditions for different classes of Pyrolysis (Peacocke & Joseph, n.d.)

	Slow Pyrolysis	Conventional Pyrolysis	Flash Pyrolysis	Fast Pyrolysis
Pyrolysis Temperature (°C)	< 400	< 450	400 - 600	> 600
Heating Rate (°C/s)	0.01 - 2	2 – 10	10 - 1000	$> 10^5$
Vapour Product Residence Time (s)	> 5	< 5	< 2	< 0.5

Coal pyrolysis may also be classified as either low temperature (<700°C), medium temperature (700°C - 900°C), high temperature (900 - 1100°C) and plasma (>1650°C). Table 2.2 illustrates the processes that occur during pyrolysis as described by Speight, 2012.

Table 2.2: Various activities that occur at different Temperature Regions of Coal Pyrolysis (Speight, 2012)

Temperature Region	Temperature Range (°C)	Reactions	Products Formed
Low	< 350	Evaporation	Water and Volatile Organics
	400 – 750		
Moderate	750 – 900	Primary Degradation	Gas, tar and liquor
High	900 – 1100	Secondary	Gas, tar, liquor and hydrogen
Plasma	> 1650	Secondary	Acetylene and Carbon Black

2.5.4 Factors affecting Coal Pyrolysis

Heating rate, temperature, pressure, particle size and coal rank are some the factors that affect coal pyrolysis (Kent, 2007).

2.5.4.1 Heating Rate

A rapid heating rate has the following effects (Kent, 2007): The liquid and gas yield is increased, hence reducing the amount of char produced. Tar with a lower H/C ratio is produced and the thermo-plasticity of coal is increased. A faster heating rate is costlier, and a complex operating system required to generate the necessary operating conditions.

2.5.4.2 Temperature

Temperature controls the placement of all atoms except carbon and hydrogen in the char, liquid and gas (Kent, 2013). A 'low' temperature (500°C - 700°C) improves the liquid yield whilst a longer residence time is required for the reaction to reach completion (Kent, 2013).

2.5.4.3 Pressure

2.5.4.3.1 Inert gas atmosphere

A high pressure reduces the reactor size as well as the tar yield. Gas-solid heat transfer is improved, but the feed mechanism and product separation processes are complicated (Kent, 2013).

2.5.4.3.2 H_2 atmosphere

The yield of liquids and lighter products are increased (Kent, 2013). However, a complex pressure control system is required and the cost of making and separating hydrogen gas, makes this process unfeasible.

2.5.4.3.3 Vacuum

Plastic behaviour of coal samples are reduced which the liquid and gas yields are increased.

2.5.4.4 Particle Size

Smaller particles are favoured, as the gas-liquid yield is improved and secondary reactions are prevented (Kent, 2013). Process is costlier due to the addition of grinding costs.

2.5.4.5 Coal Rank

A bituminous coal normally has a high volatile content and it produces large quantities of tar, whereas lignites are rich in oxygen functional groups (Kent, 2013).

2.6 Commercial Coal Pyrolysis Processes

There are many commercially existing coal pyrolysis processes. The afore-mentioned factors such as heating rate, temperature, pressure, particle size and coal rank affect the efficiency and product yield (Kent, 2013). Other factors that affect these pyrolysis processes include reactor type, process mechanics and coal residence time (Lee et al., 2015).

2.6.1 TOSCOAL Process

Preheated coal and preheated ceramic balls are fed into a rotating drum wherein flash pyrolysis occurs. The ceramic balls are preheated to a temperature of 425°C - 540°C by burning some product gas (Lee et al., 2015). The hydrocarbons, water vapour and gases released in a rotating drum, where the coal is contacted with hot ceramic balls. A trommel screen is used to separate the balls, to re-cycle to a pre-heater (Lee et al., 2015).

Some advantages include:

- It is a continuous process, thereby saving time and increasing overall throughput.
- The process utilizes an indirect heat source, which yields gas with a high heating value.
- A high throughput of solid product is achieved per unit of retort.
- Overall process design allows for easier pollution control.

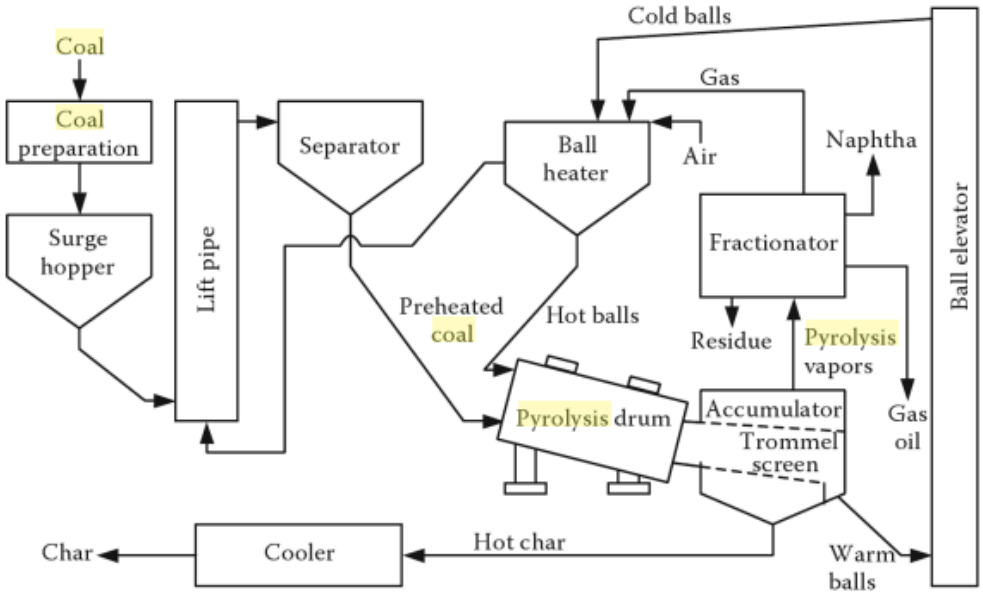


Figure 2.7: Flow diagram of the TOSCOAL Process (Lee et al., 2015)

2.6.2 Char Oil Energy Development Process

The COED process is based on fluidization technology. Initially, prepared coal is fed into the first of four consecutive fluidized bed reactors operating between 315°C - 345°C (Lee et al., 2015) to commence the pyrolysis process. Thereafter, the coal is transferred to the remaining reactors each operating at 425°C - 455°C, 540°C and 870°C respectively (Lee et al., 2015). Temperatures are selected based on the maximum temperature the feedstock can be heated to without solidifying into lumps. The energy required to drive the process is provided by combusting the char in the 4th stage with a steam oxygen mixture (Lee et al., 2015). The hot gas (fluidizing medium) flows counter currently through the stages. Vapour that is produced in the first and second stages is then transferred to a cyclone to separate out the fines. The vapour is then quenched and decanted to produce oil and gas. Gas is desulphurized and thereafter the steam is reformed producing hydrogen and fuel gas (Lee et al., 2015). Crude oil is produced from the oil by dehydrating, filtering and hydro-treating to remove nitrogen, sulphur and oxygen (Lee et al., 2015).

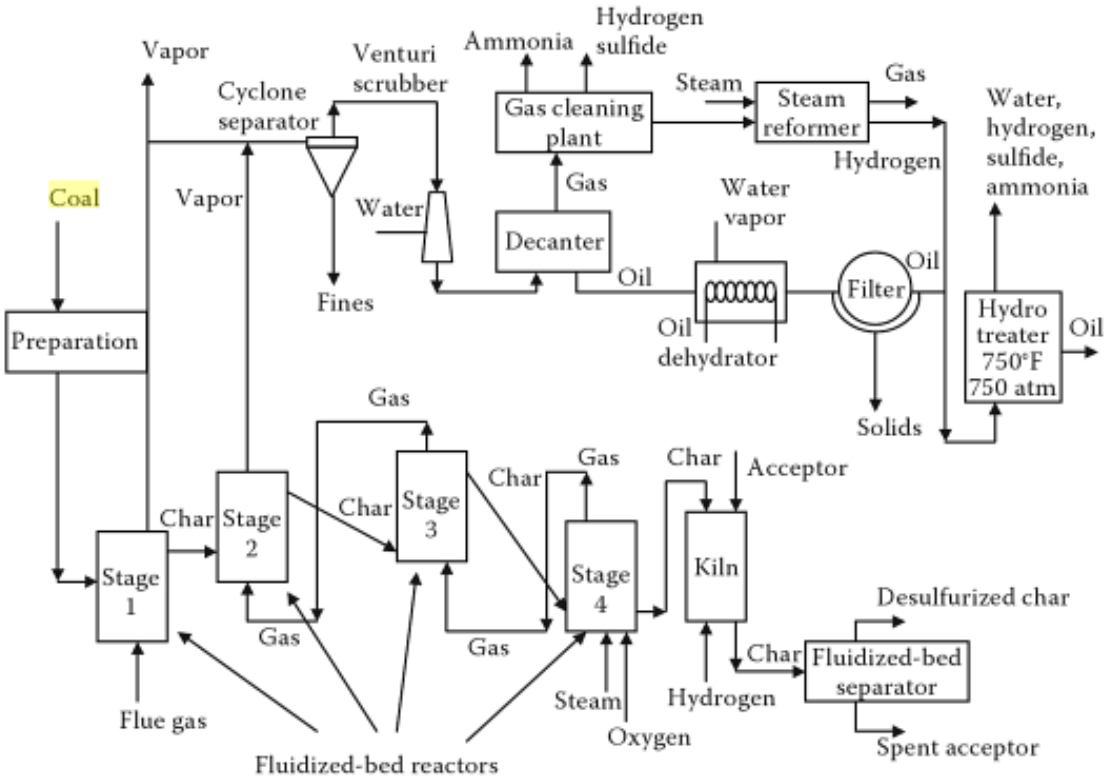


Figure 2.8: Flow diagram of the COED Process (Lee et al., 2015)

2.6.3 Lurgi-Ruhrgas Process

This is a low-pressure process created to produce liquid from low rank coals (Lee et al., 2015). Initially, crushed coal and preheated char are combined in a mixer to quickly heat the coal via direct contact to 450°C - 600°C (Lee et al., 2015). The char is preheated by partial oxidation in an entrained flow reactor (Lee et al., 2015). Product gases are transferred to a cyclone to remove the fines after which the gas is condensed. The liquid product is collected by a series of condensers. Liquid products are upgraded by partial condensation (Lee et al., 2015). A high gas yield is achieved due to the relatively long residence time. Both, primary and secondary gas products are formed. Secondary products are formed by thermal decomposition of primary products derived directly from coal (Lee et al., 2015).

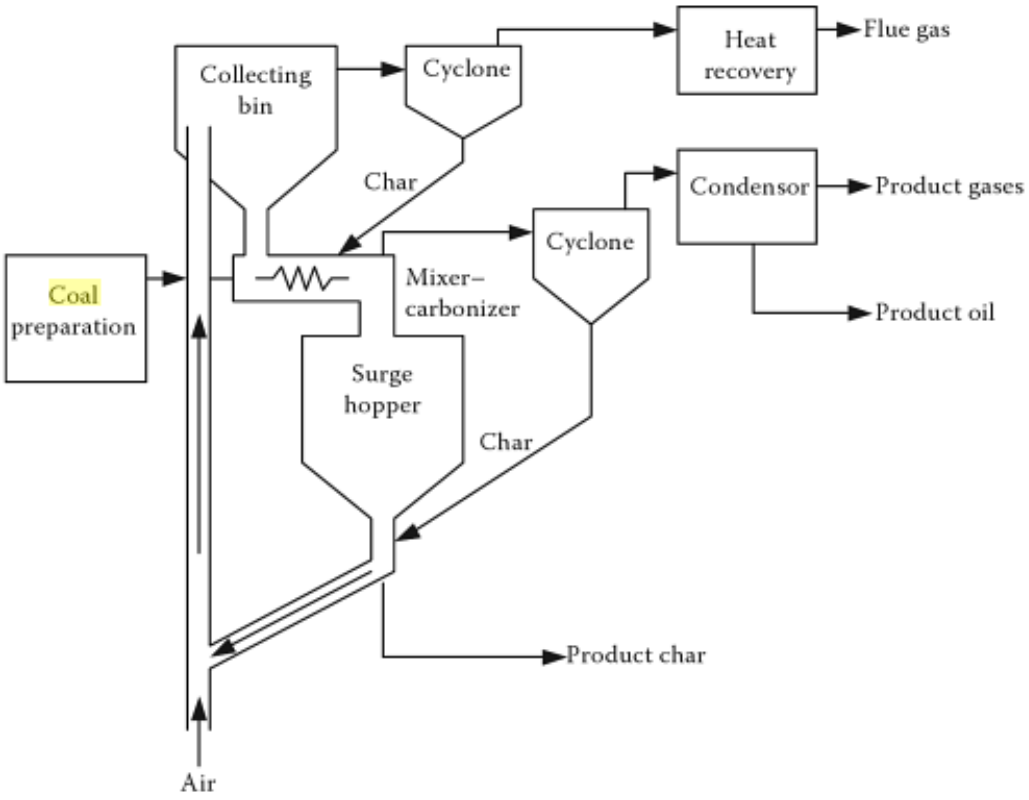


Figure 2.9: Flow diagram of the Lurgi-Ruhrgas Process (Lee et al., 2015)

2.6.4 Occidental Flash Pyrolysis Process

Ground coal undergoes flash pyrolysis utilising heat provided by hot recycle char in an entrained flow reactor (Lee et al., 2015). The reactor is operated at temperatures up to but not exceeding 760°C (Lee at al., 2015). The short residence time promotes liquid production as well as allowing for a large throughput of coal (Lee et al., 2015). Thereafter, the gas is transferred to a cyclone in order for fine char particles to be removed. The gas is quenched in a two-stage collector system whereby the first stage operates at 99°C to remove the heavier hydrocarbons (Lee et al., 2015). Quenching in the second stage operates at 25°C to remove water and light oils (Lee et al., 2015).

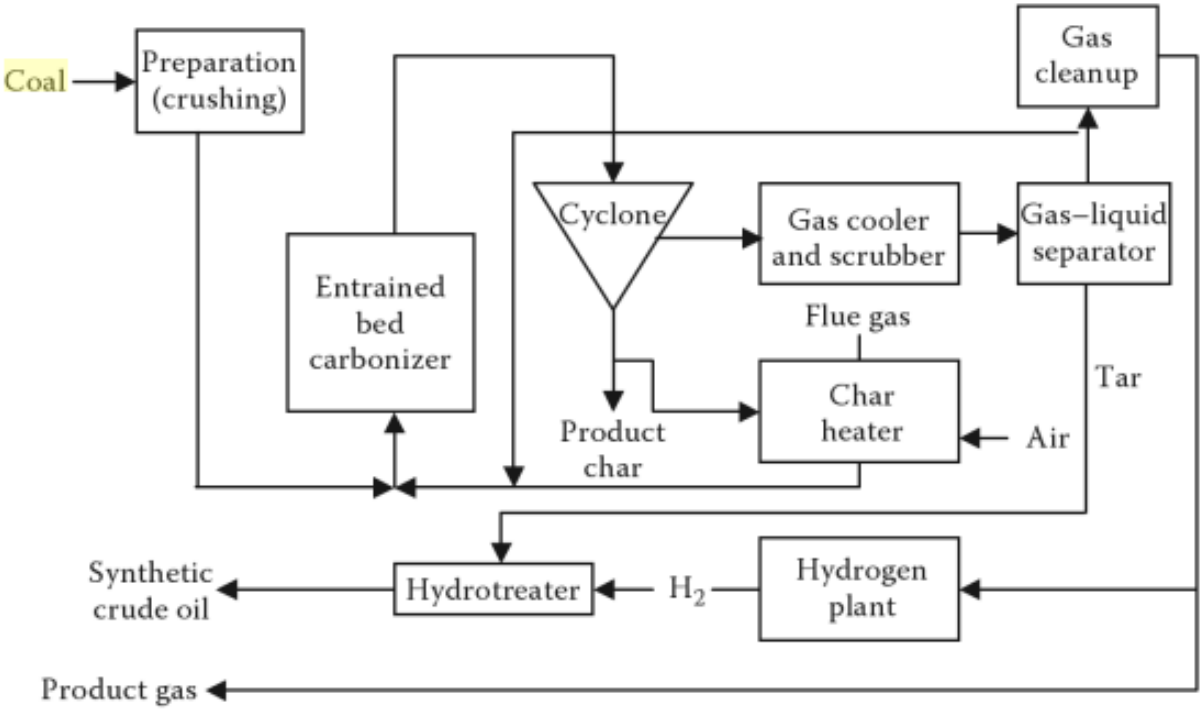


Figure 2.10: Flow diagram of the Occidental Flash Pyrolysis Process (Lee et al., 2015)

Table 2.3 provides a summary of some important information from various pyrolysis processes.

Table 2.3: Summary of various Pyrolysis processes as adapted from Speight, 2012.

Process	Reactor Type	Reaction Temperature (°C)	Reaction Pressure (psi)	Coal Residence Time	Yield (% w/w)		
					Char	Oil	Gas
Toscoal	Kiln-type retort	425-540	15	5 min	80-90	5-10	5-10
COED	Mulitiple fluidized bed	290-815	20-25	1-4 h	60.7	20.1	15.1
Lurgi-Ruhrgas	Mechanical mixer	450-600	15	20 s	55-45	15-25	30
Occidental Flash	Entrained flow	580	15	2 s	56.7	35	6.6

2.6.5 Comment on using existing processes for Pyrolysis of Waterberg Coal

The aim of this research is to investigate a way of recovering volatile material from Waterberg coal with a high ash content. The above processes were designed for treating coal with a low ash content (up to 25%) (Lee et al., 2015) and they are not suitable for treating Waterberg coal. The char will not be a saleable product and combustion of the char is required to provide the energy for heating the feed. However, these processes provided some ideas on how energy can be exchanged between streams.

2.7 Coal Combustion

Due to the variable nature of coal, the process of combustion becomes very complex. Raw coal decomposes into char and volatiles. The following equations provide an overall summary of the most significant reactions that occur (Toporov, 2015):

$$\text{Coal (raw)} \rightarrow \text{Char} + \text{Volatiles} + H_2O \qquad (2.7.1)$$

$$\text{Volatiles} + O_2 \rightarrow CO + H_2O + SO_2 + NO \qquad (2.7.2)$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \qquad (2.7.3)$$

$$\text{Char} + \frac{1}{\phi}O_2 \rightarrow (2 - \frac{2}{\phi})\,CO + (\frac{2}{\phi} - 1)\,CO_2 \qquad (2.7.4)$$

$$\text{Char} + CO_2 \rightarrow CO + CO \qquad (2.7.5)$$

$$\text{Char} + H_2O \rightarrow H_2 + CO \qquad (2.7.6)$$

Figure 2.11 shows the physical and chemical processes that occur during the combustion process.

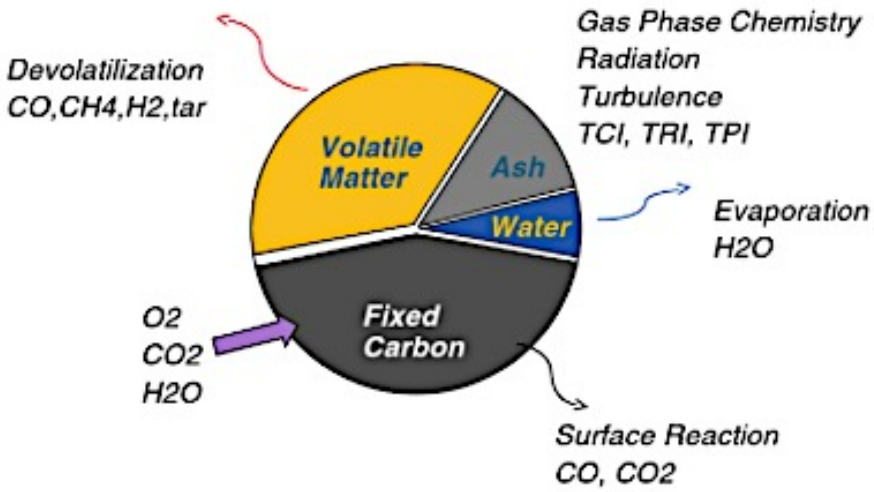


Figure 2.11: Physical and Chemical Processes occurring during Combustion (Modest and Haworth, 2016)

2.7.1 Char Combustion Reactions

2.7.1.1 Char-O_2 Reaction Models

The oxidation of char can be described by the following equation (Toporov, 2015):

$$\text{Char} + \frac{1}{\phi} O_2 \rightarrow (2 - \frac{2}{\phi}) \text{CO} + (\frac{2}{\phi} - 1) \text{CO}_2 \qquad (2.7.7)$$

whereby $\phi = \frac{2p+2}{p+2}$ is the oxidiser-to-fuel ratio. This implies that the composition of the reaction products can only have value between 1 and 2. The molar ratio between carbon monoxide and carbon dioxide is correlated to an Arrhenius equation:

$$p = \frac{[CO]}{[CO_2]} = A_0 e^{-B_0/T_p}$$

with $A_0 = 2500\ and\ B_0 = 6240\ K$ (Toporov, 2015) for particle diameter less than $50\mu m$. However, for particle diameters > 1mm $\phi = 1$. Interpolation is required for intermediate diameters.

The ratio between CO and CO_2 can also be described as follows:

$$\frac{[CO_2]}{[CO]} = A_0 p_{O_{2,s}}^{\eta_0} e^{-B_0/T_p}$$

with $A_0 = 0.02, B_0 = 30370\ K$ and $\eta_0 = 0.21$ (Toporov, 2015). $\phi = \frac{1+\psi}{2}$, where $\psi = \frac{\frac{CO_2}{CO}}{1+\frac{CO_2}{CO}}$.

2.7.1.2 Shrinking-Core Model for Solids of Unchanging Size

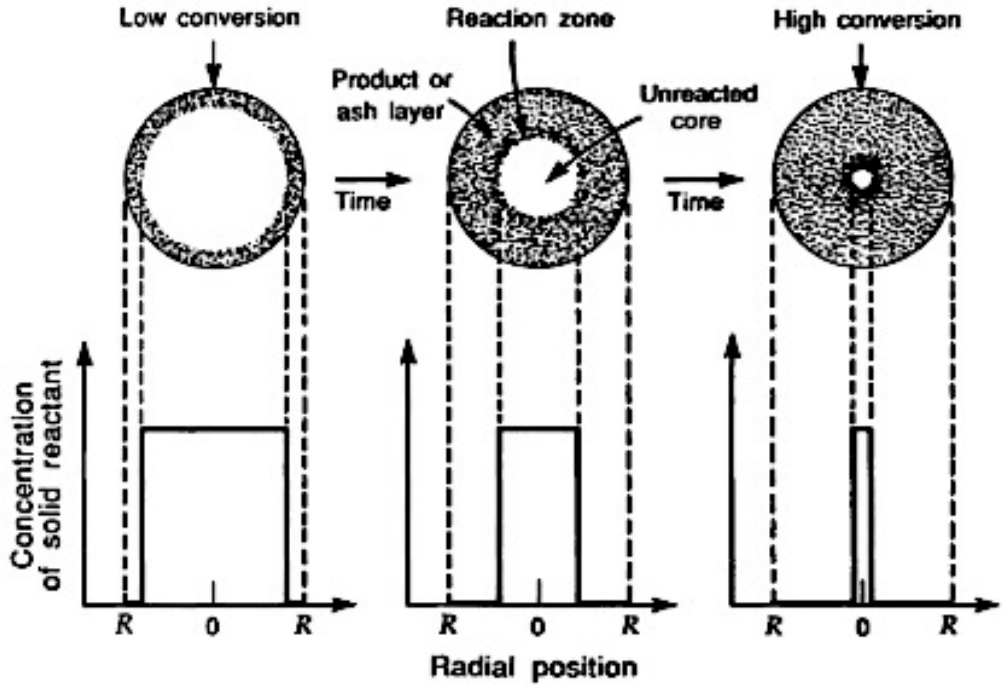


Figure 2.12: Shrinking-Core Model for Solids (Kunii and Levenspiel, 2012)

Figure 2.12 shows how the reaction proceeds over time, when coal reacts with air. It should be noted that the coal particles may form a porous structure during pyrolysis and hence it is not known if the structure of the char is porous.

Combustion of a non-porous particle can be described as follows (Kunii and Levenspiel, 2012):

- Gas diffuses through the film surrounding the particle to the surface of the particle.
- The gas then diffuses through the solid to the reaction front.
- The gas then reacts with reactant in the narrow reaction zone.
- The reaction products diffuse through the product layer to the particle surface.
- Gaseous products then diffuse into the main gas stream.

The shrinking-core model is based on these assumptions (Kunii and Levenspiel, 2012):

- Reactions are irreversible.
- Particles are spherical.
- Reaction zones are small when compared to the particle size.

2.7.1.3 Random Pore Model

The random pore model is based on the following assumptions (Bell et al., 2011):

- The weight and pore structure of the sample changes with time.
- Initially, the reaction rate increases and then decreases
- Surface reactivity is directly proportional to surface area.
- Particle diameter is constant.

2.8 Staged Coal Conversion Process

Traditional coal combustion methods utilize the hydrogen-rich (fuel) components of coal, which are driven from the coal by the high temperature. Hence, the gas stream leaving the combustion chamber will contain pollutants (e.g. sulphur, partially combusted tar, etc.) which are difficult to remove. Special removal methods are required which increase the operating costs.

Staged conversion processes for coal which is a two-stage process which combines coal pyrolysis and subsequent combustion, were developed. Figure 2.13 shows coal which first undergoes pyrolysis, where the volatiles are extracted, cooled and then sent for further

processing (upgrading). The char then undergoes combustion, which generates energy to drive other processes. The ash could be used for the manufacture of building materials (Kopanos et al., 2017).

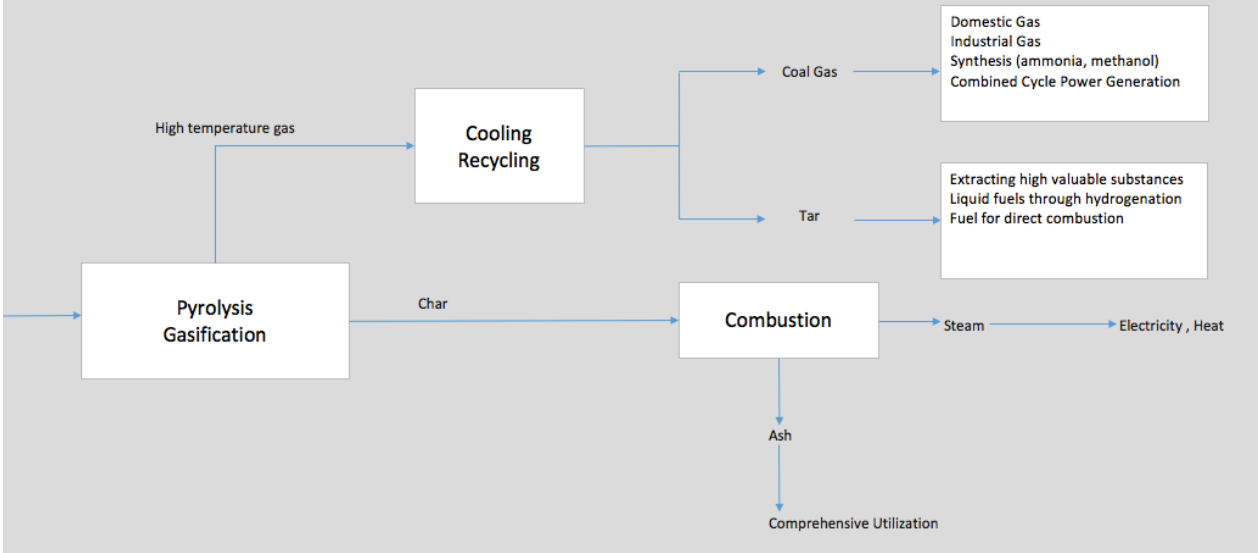


Figure 2.13: Amalgamated Pyrolysis and Combustion Process (Kopanos et al., 2017)

The process has the following advantages (Kopanos et al., 2017):

- Has a high thermal efficiency since the heat required for pyrolysis comes from the combustion of coal and the overall heat loss is also reduced.
- It is applicable to a wide range of coals.
- Some of the pollutants such as sulphur and nitrogen form a part of the pyrolysis gas stream (products). The amount of pollutants in the exiting flue gas stream is reduced.
- The process is adaptable and can be varied to generate maximum profit.

2.9 Pyrolysis Oil (Condensed Volatile Product)

The different methods of gas liquefaction allow for the manufacture of varied range of products from the syngas. There are many products different products that can be made from syngas. The process conditions determine the type of liquid fuels that are produced. The broad categories are as follows: Coke and Coke Breeze, Light Oil, Gas, Chemicals and Tar (Schweinfurth, 2009).

2.9.1 Upgrading of Liquid Products

The products with a high hydrogen to carbon ratio are normally more desirable (Speight,1994). The following processes are used to upgrade the liquid products (Speight, 1994):

- The main components of coal tar light oil include benzene, toluene, xylene (BTX), minor quantities of aromatics, paraffin's, napthenes, phenols, sulphur and nitrogen.
- Steam distillation is applied to refine benzole and remove all compounds having a boiling point lower than benzene.
- Higher boiling fractions contain pyridine bases, naphthas and coumarone bases.
- Phenols and phenol containing compounds must be removed as it affects naphathalene recovery.
- Tar acids and bases must be removed so that, solvent and heavy naphtha can be obtained from the 150°C-200°C fraction.
- The main chemical extracted from temperatures > 250°C is crude anthracene.

2.9.2 Commercial Applications of Liquid Products

2.9.2.1 BTX (Benzene, Toluene, Xylene)

BTX (Sweeney and Bryan, 2000):

- Are the lowest molecular-weight aromatic homologues.
- Does not have any commercial value.
- Forms an important component in crude mixtures (Reformate or Pyrolysis Gasoline).
- Can also be broken down into constituent compounds for separate use.
- Benzene can be used to manufacture polystyrene, ABS and phenolic resins.
- Toluene is used for making polyurethanes.
- Xylene can be used for polyester resins and fibres.

2.9.2.2 Phenols

Phenols are a very important commercial commodity and have a wide range of applications in the petroleum, paint, explosive, rubber plastics and pharmaceutical industries (Stellman, 1998). Generally, they are removed from the liquid product by using solvent extraction.

Phenols have a multitude of uses (Stellman, 1998) such as:

- Antioxidants
- Disinfectants
- Tanning agents
- Additives to lubricants and gasoline
- Manufacture dyes, colorless or light resins.
- Disinfectant for toilets, floors and drains.
- Extractive solvent in petroleum refining.
- Used to produce phenolic resins, BPA and caprocalum

2,4 Dimethyl phenol is used to manufacture:

- Pharmaceuticals
- Plastics
- Pesticides
- Rubber Chemicals

Cresols can be used in the explosive and agricultural industries.

2.10 Summary

Following the literature review, the following conclusions were reached regarding the Waterberg Coal Field:

- The Waterberg Coal Field is a major resource and every effort should be made to recover as much value from the resource as possible. This includes processing more seams while mining is in progress and making mining of the deep seams more attractive.
- A significant quantity of coal with a high mineral content is probably discarded during the mining of selected seams. This coal can be recovered at low cost in open cut mining.

- A significant quantity of coal (with a high mineral content) is probably discarded during upgrading of Waterberg coal.
- Hence a process for recovering value from coal with a high mineral content is desirable.
- Pyrolysis appears to be the best option, using combustion of the char to provide the energy for pyrolysis. This process does not require water and the residue, after combustion, is suitable for discarding. Heat exchange between the incoming and exiting streams can be used to minimise the disadvantage of a high mineral content in the feed.

Chapter 3

Equipment Review and Experimental Procedure

3.1 Design of Chemical Extraction Unit

The scope of this project included the proposed design of a unit to enable efficient and feasible extraction of chemicals from coal. A mass and energy balance was conducted over the system on conclusion of experimentation, to provide an indication of the feasibility and viability of this project.

There are many factors that should be considered when designing an extraction unit (reactor).

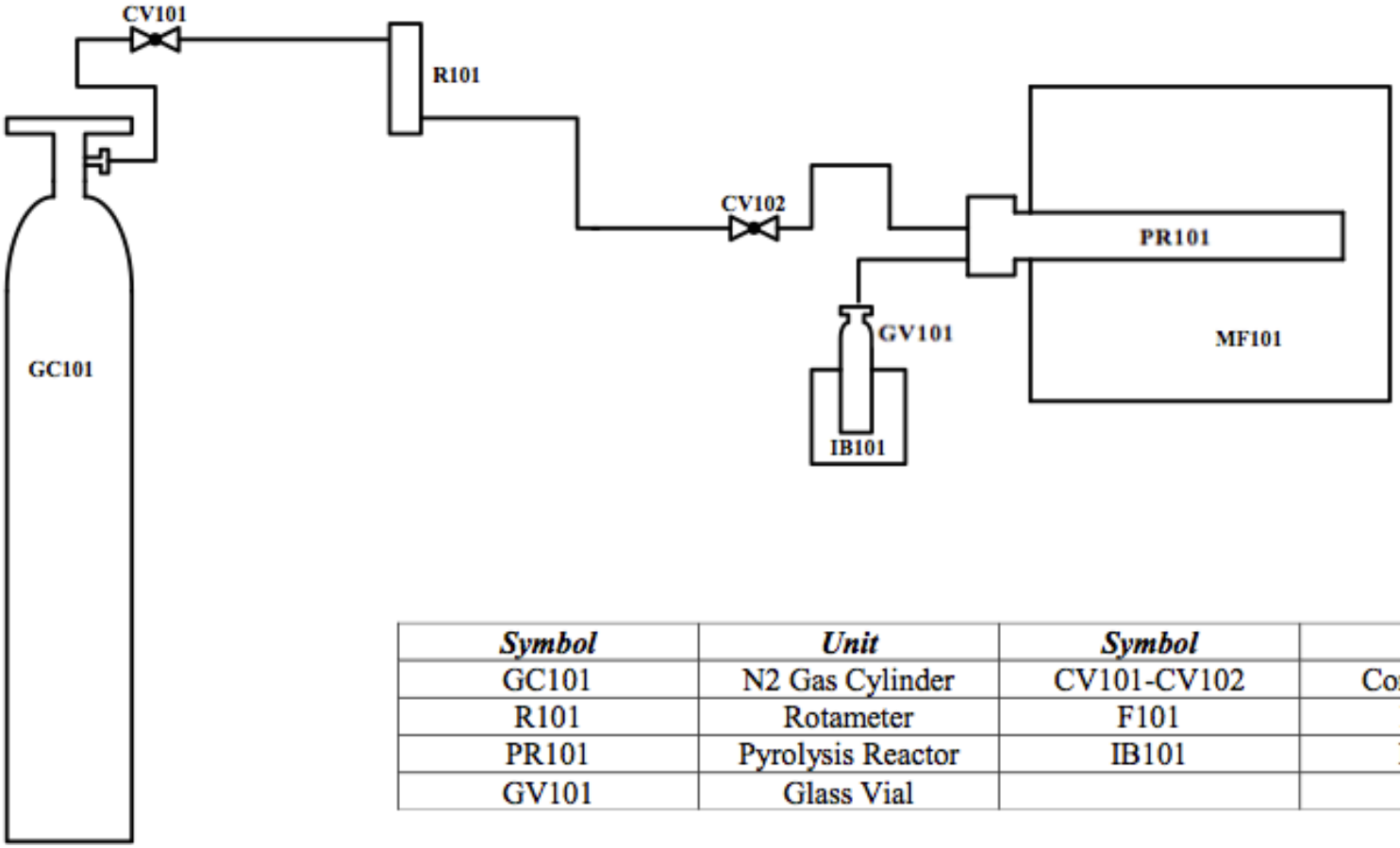
These include:

- Choice of reactor - Industrial reactor design should satisfy the following criteria: chemical factors (reaction kinetics), mass transfer factors, heat transfer factors (addition or removal of heat) and safety factors (hazardous substances) (Sinnott, 2005).
- The operating temperature and pressure.
- The nature of the environment within which the experiment is conducted i.e.: inert or hydrogenated.
- The type and size of the feedstock material.

In order to meet the aims and objectives of this project, experiments simulating the conditions of pyrolysis and combustion described within the proposed extractor unit design were conducted.

3.2 Experimental Setup

3.2.1 Pyrolysis Liquid Extraction System



Symbol	*Unit*	*Symbol*	*Unit*
GC101	N2 Gas Cylinder	CV101-CV102	Control Valve
R101	Rotameter	F101	Furnace
PR101	Pyrolysis Reactor	IB101	Ice Bath
GV101	Glass Vial		

Figure 3.1: Process Flow Diagram of Experimental Unit

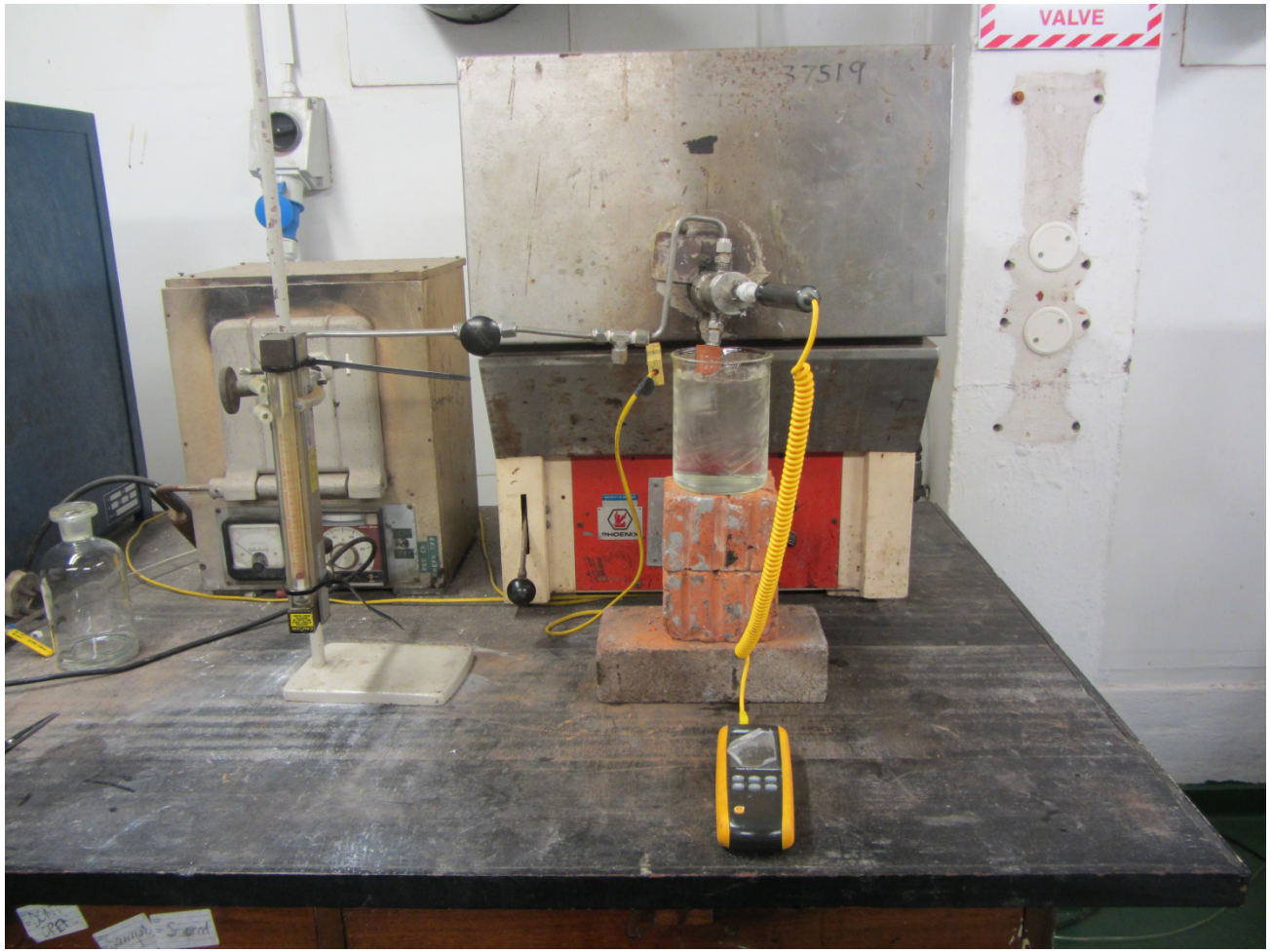


Figure 3.2: Laboratory Setup

Figure 3.1, shows the process flow diagram for the experimental setup whilst Figure 3.2 shows a photograph of the laboratory setup.

Firstly, the pyrolysis reactor (PR101) was loaded with the prepared coal sample. In view of the fact that the rate of pyrolysis and the subsequent rate of combustion will be limited by diffusion through a porous residue, all the tests were done on pieces of coal which were envisaged as the top size of the coal fed to the reactor. This also ensured that the heat and mass transfer was available from all sides of the particle.

The reactor was sealed and attached to all necessary piping. A thermocouple was also placed inside the reactor to monitor the reactor temperature. A glass vial (GV101) was attached to the exit pipe of the reactor to collect the pyrolysis gas. The 'pyrolysis gas' was collected and cooled by immersing the glass vial in an ice water bath (IB 101).

A controlled flow of nitrogen gas was used to carry the gas released during the pyrolysis reaction from the reactor into the glass vial. The calibration curve for the mass flow controller can be seen in Appendix A.

3.2.2 Equipment Review

3.2.2.1 Nitrogen Gas Cylinder

A 99.999 % purity Nitrogen cylinder was supplied by Afrox and was used as received.

3.2.2.2 Thermocouple Thermometer and Thermocouple Probe

A K-Type Thermocouple, Dual Input, -50°C ~ 1300°C (MT 632) and a custom made 0.5 m k-type thermocouple probe was purchased from MAJORTECH. The k-type thermocouple was selected as it is able to withstand temperatures up to 1260°C. It has an accuracy of +/- 2.2°C. The thermocouple had a 316SS sheath, capable of withstanding the high operating temperatures (Sinnott, 2005).

3.2.2.3 Glass Vials

Borosilicate glass vials were used for collection of volatiles (hydrocarbons and water).

3.2.2.4 Mass Balances

An Analytical OHAUS balance (PA214) was utilised for measurements with a maximum capacity of 210g (glass vials) whilst a METTLER TOLEDO balance was used for heavier equipment (reactor) with a mass of 0 – 20 kg.

3.3 Pyrolysis Reactor Design

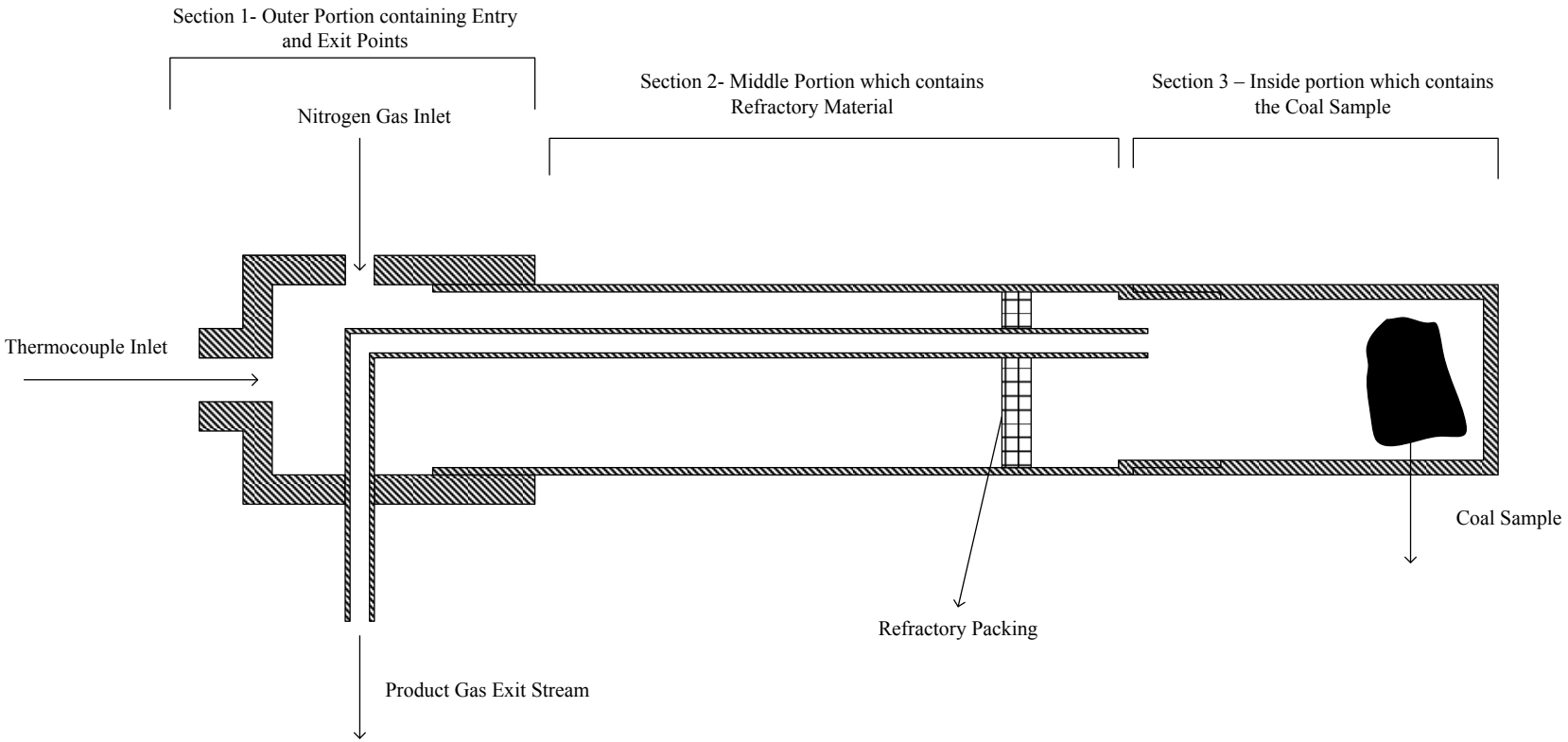


Figure 3.3: Simplified Cross Section of Laboratory Pyrolysis Reactor (The thermocouple sheath also protrudes into the reaction zone)

3.3.1 Reactor Design

Prior to designing the reactor, the following factors were taken into consideration:

- The temperature that it would have to withstand.
- Easy access to load and remove sample.
- Effective manner to extract the product.

The reactor had to be designed in order to facilitate efficient movement of gas, thereby enabling maximum collection of valuable pyrolysis liquid.

The reactor was made of stainless steel which can withstand temperatures of up to 1100°C (Sinnott, 2005). The coal piece was cut, sized and loaded into the reactor. The back portion of the reactor was detachable to ensure easy loading of the coal piece.

The reactor has three openings as seen in Figure 3.3, the first allows space for the thermocouple tube to be inserted into the reactor, the second is an entry point for the nitrogen gas and the third is an exit point for the gas released during the pyrolysis reaction. The thermocouple tube occupied a central position, which allowed it to extend to a position near the sample. The tube for the exit gas was therefore in an off-centre position.

The reactor was fabricated in three parts namely: Section 1, Section 2 and Section 3. Section 1 was the part of the reactor which remained outside the furnace therefore it was made with thicker walls to prevent major heat losses to the environment. Sections 2 and 3 were the two parts that entered the furnace. Section 2 houses the refractory packing which reduces radiant heat transfer to the main body of the reactor, and directs the products of pyrolysis into the exit gas tube. Section 3 contained the coal sample.

It is also important to note that sections 2 and 3 have thinner walls allowing for easier heat transfer into the reactor.

3.4 Experimental Procedure

Prior to commencing any of the subsequent steps the furnace was turned on and set to the necessary temperature.

3.4.1 Preparation and Cleaning of Equipment

Before setting up the experimental system as illustrated by Figure 3.1, it was important to clean all piping, valves, glassware and equipment (reactor). This was to remove any residue (remaining tar), dirt or impurities that may have been present to ensure that accurate data was collected. All components were flushed through and wiped with the acetone and then left to dry.

3.4.2 Assembling the Experimental Setup

The system was setup as shown by Figure 3.1. The rotameter was first attached to a clamp thereafter the piping was attached. PTFE tape was used to seal the pipe thread thus preventing leaks. The valve was attached to the system along with the necessary piping. The reactor was not attached at this point.

3.4.3 Coal Sample Preparation

Coal samples were obtained from Waterberg coalfield mines. An assortment of unclassified samples was received. Hence, they were selected on the basis of their colour and hardness. Figure 3.4 is an illustration of a black, shiny sample, which appeared to be vitrinite, with different layers, some of which were very brittle. Figure 3.5 is an example of a dull grey sample, which was relatively hard and it had distinct layering. A band-saw, was used to cut the samples into suitably sized pieces. The samples were weighed and the initial mass was recorded.

Figure 3.4: Shiny and Brittle Coal Sample

Figure 3.5: Dull and Hard Coal Sample

3.4.4 Preparation and Loading of the Reactor

Firstly, the reactor was dismantled into its constituent parts in order to wash the entire apparatus with acetone. From the opening at the front of the reactor the thermocouple was inserted as shown in Figure 3.3 and the opening was sealed. The reactor-thermocouple system was weighed and the mass was recorded.

The coal sample was placed inside the reactor after the weight was recorded as shown in Figure 3.3. The removable back part of reactor which contained the coal sample, was then screwed onto the body of the reactor. In order to prevent the thread from seizing, during the heating process, an anti-seize paste was applied.

The tubes entering and leaving the reactor were then joined to the gas supply, collection flask, etc. which were supported using clamps.

3.4.5 Product Collection

The product was collected in glass vials. After cleaning, the vial was weighed and the mass recorded. A rubber stopper with a hole having the same diameter as the piping, was used to attach the vial to the product collection point as shown on Figure 3.3.

3.4.6 Condensation of Product Gas

The vial was placed in an ice water bath to cool the gas to a liquid. The ice water bath comprised of ice placed within a glass beaker.

3.5 Pyrolysis and Combustion Experimental Procedure

3.5.1 Pyrolysis

Four different types of experiments were conducted their results were recorded and observations noted.

They were as follows:

- Preliminary pyrolysis experiments were conducted on 'Large' pieces of coal, (about 25mm x 30mm x 50mm). The temperature was raised in 100°C intervals, from 300°C to 700°C, with a half-hour period at each temperature. The recovery of volatiles at each temperature was noted.

  The subsequent combustion experiments revealed that a core of unreacted char was present in the high-ash samples. *It was therefore decided that <u>all</u> further tests would be done on smaller pieces of coal (about 25mm x 25mm 30mm).*

- Repeat tests over a temperature range of 300°C - 700°C. (Using the new particle size)

- Tests at a temperature of 700°C for 1 hour.

- Tests at a temperature of 700°C for 30 minutes.

3.5.1.1 Preliminary tests using a temperature range of 300°C - 700°C ('Large' pieces)

After completing all of the steps discussed above the following procedure is observed for this experiment:

Once the furnace has reached the first temperature of 300°C the reactor was inserted through the 'window' of the furnace door, and the flow of nitrogen was set at 10 ml/min. The reaction was allowed to proceed for 30 minutes, after which the reactor was removed and the vial was replaced to collect product at 400°C. Whilst the furnace was reaching the new set temperature of 400°C, the reactor was wrapped in insulating glass wool and the openings were stoppered to prevent air from entering the system. When the furnace reached the new set temperature of 400°C the reactor was placed inside and the reaction was allowed to proceed. This process continued for temperatures of 500°C, 600°C and 700°C respectively.

An examination of the data from the pyrolysis experiments revealed a disturbing 'loss' of volatile material. It was finally concluded that some of volatile material had condensed in the cooler parts of the reactor, which extended outside the furnace. The problem was solved by weighing the reactor-thermocouple system, to record the change in mass. However, the tarry substance was then not removed and therefore could not be analysed.

3.5.1.2 Repeat tests on smaller coal pieces over a range from 300°C - 700°C

This experiment followed the same procedure as above. However, the mass of the coal pieces was reduced substantially, to ensure that the reactions were completed. The sample mass was in the range 7g to 23.5g, while the previous experiments were conducted on coal pieces with a mass of about 40g.

3.5.1.3 Tests at a temperature of 700°C for 1 hour

The procedure and approximate sample masses were the same as those used in 3.5.1.2, but the reactor was only inserted when the furnace temperature reached 700°C. The timer was set for one hour but the vials were changed every 15 minutes to observe the amounts collected for each time period.

3.5.1.4 Tests at a temperature of 700°C for 30 minutes

When the furnace reached 700°C, the reactor was inserted and the reaction was allowed to proceed. The timer was set for 30 minutes and the volatiles were collected in a single vial.

3.6 Post Experimentation

The valves controlling gas flow through rotameter was turned off and the nitrogen gas cylinder was closed. The ice water bath was removed. The reactor was removed and placed on refractory bricks to cool overnight. The furnace was also switched off.

The day after the experiment was conducted, the sample contained within the pyrolysis reactor was removed and weighed and the mass was recorded. The glass vials containing the liquid product were also weighed.

3.6.1 Samples for Analysis

In the first set of experiments product samples were only collected in the glass vial. Only after inspection of the mass and energy balance, it was observed that a large mass was unaccounted for, this tarry substance was found to have condensed within the reactor.

Therefore, for the second and third sets of experiments samples were also taken from within the reactor tube. This product sample was obtained washing the tube with 10ml of ethanol.

Product samples were collected in the glass vials during the pyrolysis reaction. It should be noted that two phases were present in the glass vial (i.e. a small amount of water was present at the bottom). A third sample set of samples was collected by washing out the reactor with 10 ml of ethanol. Karl Fischer and GCMS analyses was performed on these samples.

3.7 Combustion Experiments

These experiments were conducted to determine how rapidly the pyrolysed samples (char) reacted with air at various temperatures. The sample was transferred to a porcelain crucible and placed in a muffle furnace. The door of the furnace was left ajar and an extractor fan provided a constant flow of air through the furnace.

The mass of the sample and crucible was measured. The sample was heated from room temperature to 300°C. This process took a total of 75 minutes. The sample-crucible system was then removed and weighed. The sample was rotated 180°, to ensure that the entire coal sample surface was exposed to the incoming air to enable efficient combustion, before it was put back into the furnace.

The oven was then set to a temperature of 400°C. The sample was then placed back to allow the reaction to proceed for the heating phase from 300°C - 400°C. This took a total of 45 minutes. The sample-crucible was then removed and weighed.

The sample was rotated 180° and then put back into the furnace for 22.5 minutes for the combustion to occur at a temperature of 400°C.

The outlined above was repeated for the following temperature ranges: 400°C - 500°C, 500°C - 600°C and 600°C - 700°C. The sample was allowed to react for 45 minutes whilst it was kept at 500°C, 600°C and 700°C for 22.5 minutes.

It was initially assumed that all the combustible material would be oxidized at 700°C, as this is the normal temperature for determining ash content, after pulverizing (Singh, 1997).

3.8 Gas Chromatography-Mass Spectrometry

GCMS is an established effective method used to analyse samples and identify compounds.

GCMS of the product samples collected was essential, as this data formed a crucial part of the mass and energy balance in Chapter 5. The data obtained provided the approximate amounts of compounds present and was used to calculated the heat capacity and other required values.

Preliminary GCMS analysis was done on the samples from the first three experiments however the method of analysis, upon consultation with an expert was deemed to be unsatisfactory. Therefore, these results could not be utilised Investigation of the sample collected in the glass showed a distinction in layers of the product, therefore a solvent should have been added or the sample could have been separated into the two layers.

For the fourth set of experiments the sample preparation was done as explained below.

GCMS Sample Preparation

On conclusion of the pyrolysis experiments, the reactor was left to cool and a sample of the residue found inside the reactor was taken by washing with 10 ml of ethanol. The samples which were collected in the glass vials were weighed and then centrifuged to split the layers (top and bottom). The top layer was extracted in hexane therefore it contained no water.

Three samples (Inside, top and bottom) were analysed for each coal sample of different ash content.

As the GCMS is a very sensitive instrument and can detect minute traces of compounds the samples were diluted to a concentration of 10 ppm.

GCMS Calibration

Firstly, the GCMS was calibrated. This was done using a blank sample, which resulted in no compounds being detected. This implied that the GCMS was ready for use to analyze the product samples. The calibration curves are not available.

GCMS Analysis

The instrument used for analysis was a GCMS from Shimadzu, the QP2010- SE with an auto sample AOC-20s and an auto injector AOC-20i.

3.8.1 Gas Chromatography Parameters

Initially, the instrument was switched on and the following parameters were set:

Temperature: An initial temperature of 70°C was set, held for 1.00 min at a rate of 5.00°C/min going to a final temperature of 280°C, held for 25.00min, giving a total run time of 68.00 minutes.

Injector Temperature: 250 °C

Injector Mode: Split

Flow control mode: Linear Velocity

Pressure: 27.3 kPa

Total Flow: 10.1 ml/min

Column Flow: 0.65ml/min

Linear Velocity: 30.0cm/sec

Purge flow: 3.0ml/min

Split ratio: 10.0

3.8.2 Mass Spectrometry Parameters

The following parameters were set:

Ion source temperature: 200°C

Interface temperature: 280°C

Detector Voltage: 0.91 kV.

Column Type: InertCap 5MS/Sil with 0.25µm thickness, length of 30 m and a diameter of 0.25µm. The amount of sample injected was 1µl, and this was passed through a glass inlet with glass wool inside, provided by Shimadzu.

3.9 Karl Fischer Analysis

Karl Fischer analysis uses titration as the method of determining water content of a sample. The Karl Fischer analysis to determine water content in a sample was done using the Mettler Toledo Easy KFV EasyPlus Titration. The presence of water in the samples decreases the value of the product. The water must be removed to upgrade the product, which leads to increased costs. Since, the viability of this process was being investigated it was essential to determine the water content.

Three samples were prepared for GCMS analysis (Inside, top and bottom). Only the bottom sample was subjected to Karl Fischer analysis. The inside sample was contained within the reactor at a temperature of 700°C, it should not contain any water (above the boiling point). The top sample was extracted in hexane which is insoluble in water.

Chapter 4

Experimental Results

It should be noted that the mass of liquid was measured in stages, as the temperature was raised, or as time progressed. However, more than half of the volatile material condensed in the reactor and the tube leaving the reactor. The change in the mass of the tube was recorded on the following day to measure the mass of this 'tarry' material. It was removed after each test using ethanol, and analysis of the ethanol solution was used in the later tests to determine the composition of the 'tar'.
The Tables reflect the combined mass of tar and liquid samples recovered externally. The Figures record the external recovery of the liquid alone, versus temperature, time, etc.

4.1 Preliminary Tests

4.1.1 Pyrolysis and Combustion of 'Large' Coal pieces at temperatures between 300°C - 700°C

The first set of experiments were conducted using 4 coal samples, approximately 50mm by 25mm by 30mm in dimension. (The methods are described in Chapter 3). The pyrolysis experiments were conducted to determine the proportion of volatiles (hydrocarbons and water) present in each sample. The combustion experiments provided the ash content as well as the percent of non-volatile combustibles (elemental carbon) present within each sample.

Table 4.1 summarizes the results for coal samples with ash content ranging from 38.55% to 75.45%, all considered to be a high ash coal. The results in Table 4.1 show that the volatile content remains relatively high as the ash content increases, and the proportion of volatile material in the non-ash fraction increases to about 50%. This supports the viability of recovering volatile material from seams in the Waterberg which have a high ash content. Overall, the recovery of volatiles was high, with some of the losses being accounted for by possible decomposition into non-condensable gases, such as methane and nitrogen. It was noted that a small amount of water was present, which formed a separate layer below the organic liquid. The amount of water was quantified in later experiments and it was postulated that it could have been produced by thermal decomposition of organic compounds.

Table 4.1: Overall Summary of Results obtained for 'Large' Coal Pieces over a temperature range of 300°C - 700°C

Initial Sample Mass (g)	% Ash	Volatiles Recovered Externally (Water + Hydrocarbons) (Mass %)	Volatiles Recovered from Reactor & Tubing after the experiment (Mass %)	Non-Volatile Combustibles (Residual Carbon) (Mass %)	% Recovery of Volatiles (Mass Balance Reconciliation)
40.6	**38.55**	2.91	18.47	39.28	96.40
33.1	**55.52**	5.54	12.99	24.85	94.52
40.1	**70.11**	0.59	13.22	14.93	98.23
48.7	**75.45**	5.24	8.01	10.59	94.92

The pyrolysis experiments on the 'large' coal samples were conducted using progressive 100°C increases in temperature from 300°C to 700°C, to find a suitable operating temperature. The pyrolysis data is summarized in Figure 4.1, which shows the amount of liquid recovered externally, relative to the original mass of the sample at each temperature. The oven temperature was kept at each selected temperature for 30 minutes, and hence the overall time for the pyrolysis test was 2.5 hours.

The sample containing 38.55% ash, produced mainly lower boiling volatiles, with boiling points occurring up to 400°C. An almost negligible quantity was recovered externally above 400°C. The 55.52% ash content sample appeared to have more volatile material with a higher boiling temperature, as the greatest mass extracted was at 500°C and a significant mass was also extracted at 600°C. The 70.11% ash content sample had volatiles mostly occurring in the 600°C temperature range. The 75.45% ash content sample behaves similarly to the 38.55% ash content sample.

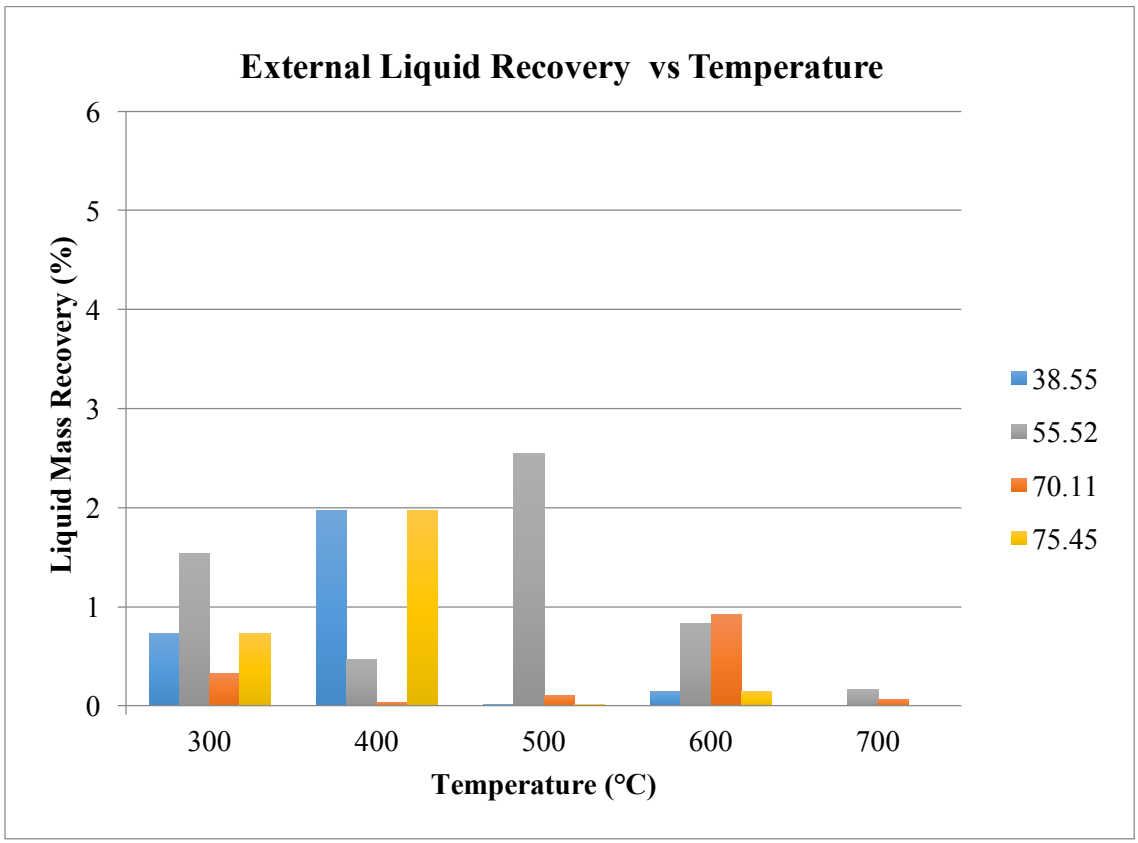


Figure 4.1: External Liquid Recovery during Preliminary Pyrolysis tests for Different Temperatures for 'Large' Coal Pieces (varying ash content) over a temperature range of 300°C - 700°C

Figure 4.2 shows the cumulative mass recovered externally over the entire temperature range of 300°C-700°C. The graph shows, for the lower ash samples, the total mass recovered was at lower temperatures whilst the higher ash content samples (70.11%) had volatiles that were extracted at higher temperatures.

The recovery of volatile material from the 38.55% ash content sample increased negligibly after reaching a temperature of 400°C, whilst it continued to increase for the 70.11% sample until 600°C, after which there was no detectable increase in the mass recovered. The 55.52% ash content sample did not reach a plateau it continued increasing up to 700°C whilst the 75.45 % sample reached a plateau at 400°C. An overall decrease in coal reactivity could be attributed to the decrease in the hydrogen content as pyrolysis progresses at higher temperatures (Odeh et al., 2017)

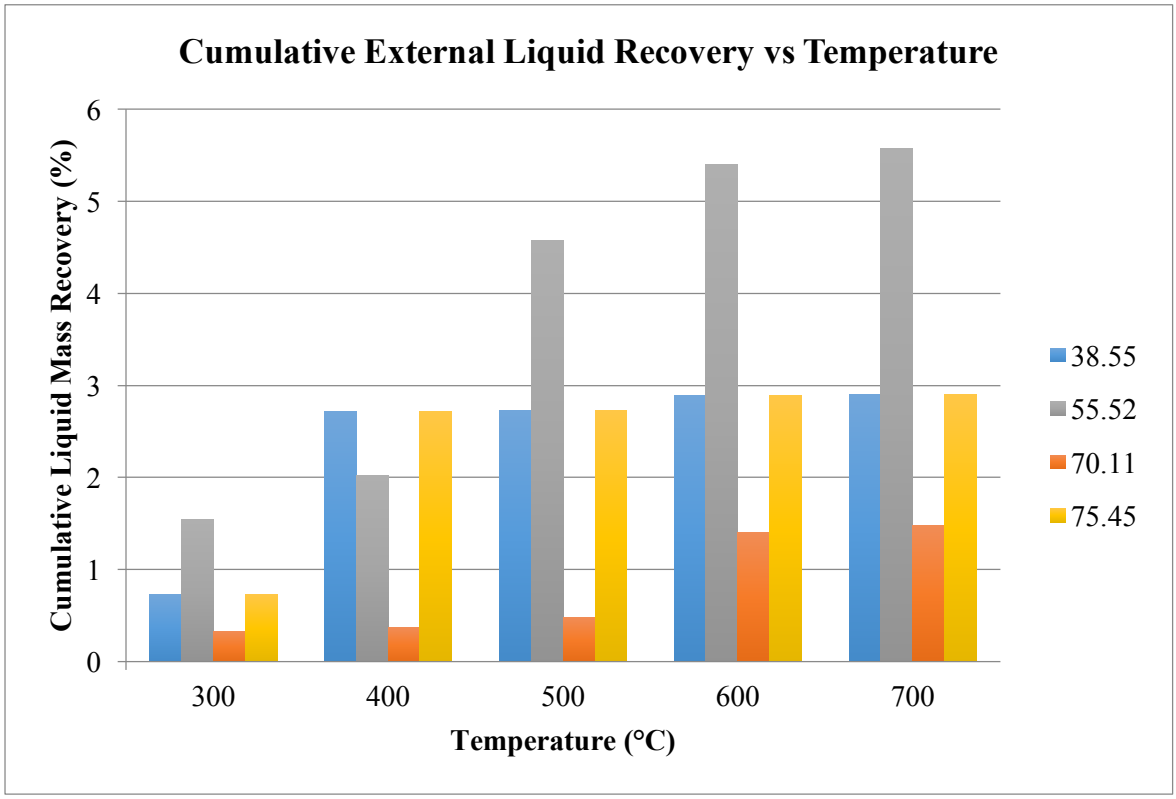


Figure 4.2: Cumulative External Liquid Recovery during Preliminary Pyrolysis tests at Different Temperatures for Large Coal Pieces (varying ash content) over a temperature range of 300°C - 700°C

Figure 4.3 was generated from the data obtained during the combustion phase of the experiments, which were also conducted for 30 minute intervals, at progressively higher temperatures. The final sample mass was assumed to be the ash content of the original sample, because 700^{o}C is the usual temperature used for determining ash content in pulverized samples. Analysis of the gradient of the graphs show that significant mass loss occurred in the 500°C-600°C and the 600°C-700°C temperature ranges.

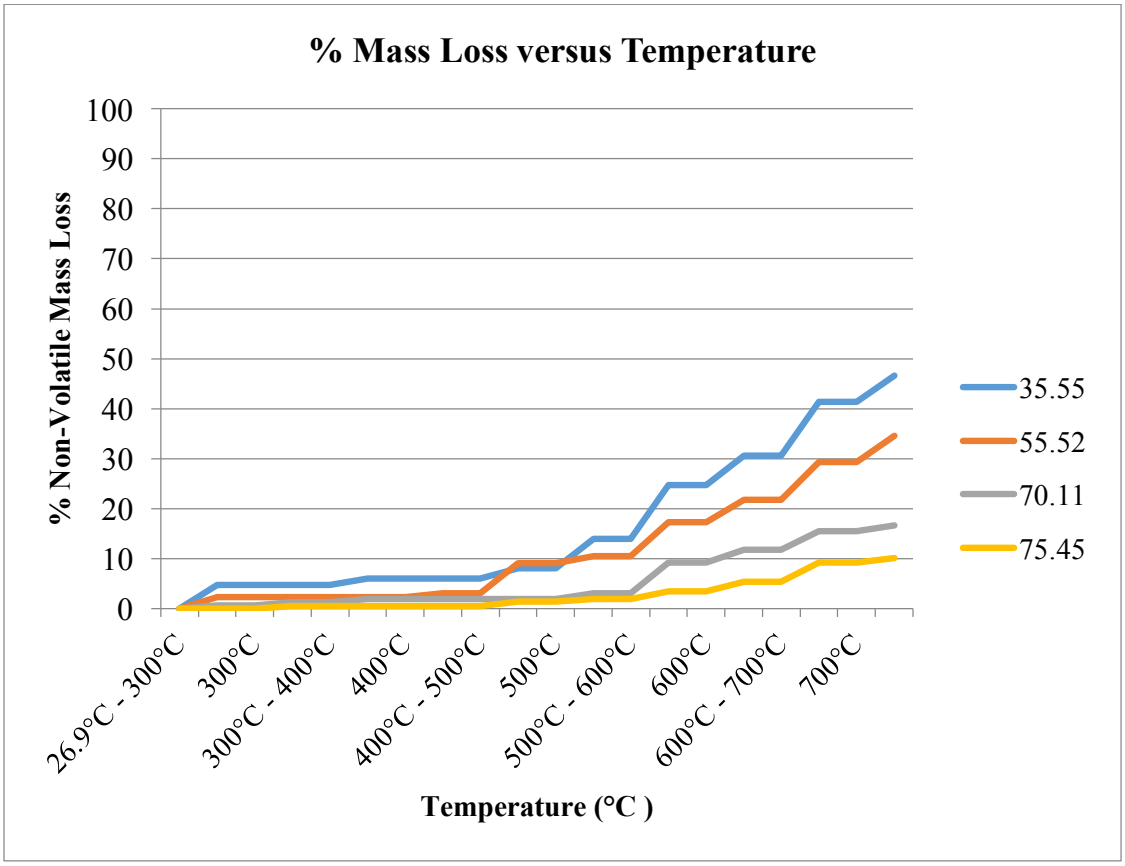


Figure 4.3: Mass Loss during Combustion for Large Coal Pieces over temperature range of 27°C - 700°C

On conclusion of the combustion experiments, the samples were left to cool and thereafter broken in half along a seam between layers. The samples with a high ash content retained their original shape and an unreacted core was observed, as shown in Figure 4.4. This suggests that the rate of oxidation was ultimately determined by diffusion through the ash layer, as explained by the shrinking core model (Kunii and Levenspiel, 2012) The size of the unreacted core varied and the plots shown in Figure 4.3 show that there was no leveling off of the mass with time. It was concluded that the maximum size of the samples for the envisaged process should be smaller and that further laboratory work should be conducted using smaller pieces of coal. It was also concluded that the initial ash content should be determined by pulverizing the residual sample and re-exposing it to air at 700^{o}C.

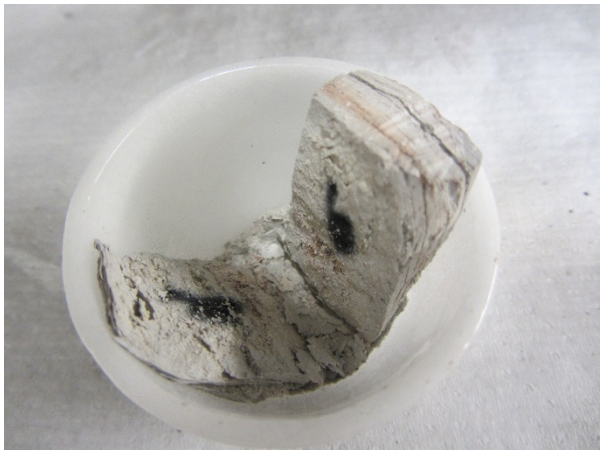


Figure 4.4: Split 'large' sample, showing the unreacted core

4.1.2 Repeat tests over a temperature range of 300°C - 700°C. (Using the new particle size)

Eight smaller pieces of coal were used in the second set of experiments with masses ranging from 7g to 23.5g, compared to the preliminary tests on 'large' pieces, which had a mass of about 40g. These experiments were a repeat of the first set of experiments, except that particle size was reduced. The experiments were conducted as described in Chapter 3.

On conclusion of the combustion experiments, the data was summarized in Table 4.2, in terms of ash content (medium-ash samples ranging from 18% - 35% and high-ash samples in the range between 67.55% - 79.10%). The same trends were observed: A decrease percent volatiles and a decrease in the residual carbon content (non-volatile combustibles) as the ash content increased. The ratio of recoverable liquid to residual carbon increased, on average, as ash content increased.

Table 4.2: Overall Summary of Results obtained for Repeat tests (Using new particle size) over temperature range of 300°C - 700°C

Initial Sample Mass (g)	% Ash	Volatiles Recovered Externally (Water + Hydrocarbons) (Mass %)	Volatiles Recovered from Reactor & Tubing after the experiment (Mass %)	Non-Volatile Combustibles (Residual Carbon) (Mass %)	% Recovery of Volatiles (Mass Balance Reconciliation)
6.98	**18.62**	1.31	31.51	47.26	96.19
9.56	**32.41**	2.55	24.05	40.78	99.19
17.72	**33.30**	4.06	20.89	40.64	95.74
8.38	**34.60**	1.19	22.67	40.57	96.12
15.40	**67.55**	1.138	15.59	14.94	96.92
13.68	**69.43**	2.82	15.35	11.69	96.26
12.29	**70.77**	0.03	12.20	16.27	94.37
23.51	**79.10**	2.37	8.93	9.36	97.91

Figure 4.5 shows the mass of liquid recovered externally, relative to the original mass of sample. Samples having an ash content ranging from 18.62 % - 34.6 % (medium ash) contain a greater amount of volatiles at lower temperatures.

The coal sample having an ash content of 18.62% has most volatiles with boiling points occurring up to 500°C, and a negligible amount was collected at 600°C and 700°C. The coal samples in the 30% range displayed a similar trend.

The coal samples with an ash content in the 60% - 70% range had a large quantity of volatiles collected externally in the higher temperature range, with most of the volatiles being collected at 600°C. A very small quantity was extracted at lower temperatures (300°C-500°C).

This trend, seen in Figure 4.5, is similar to those observed in similar to Figure 4.1.

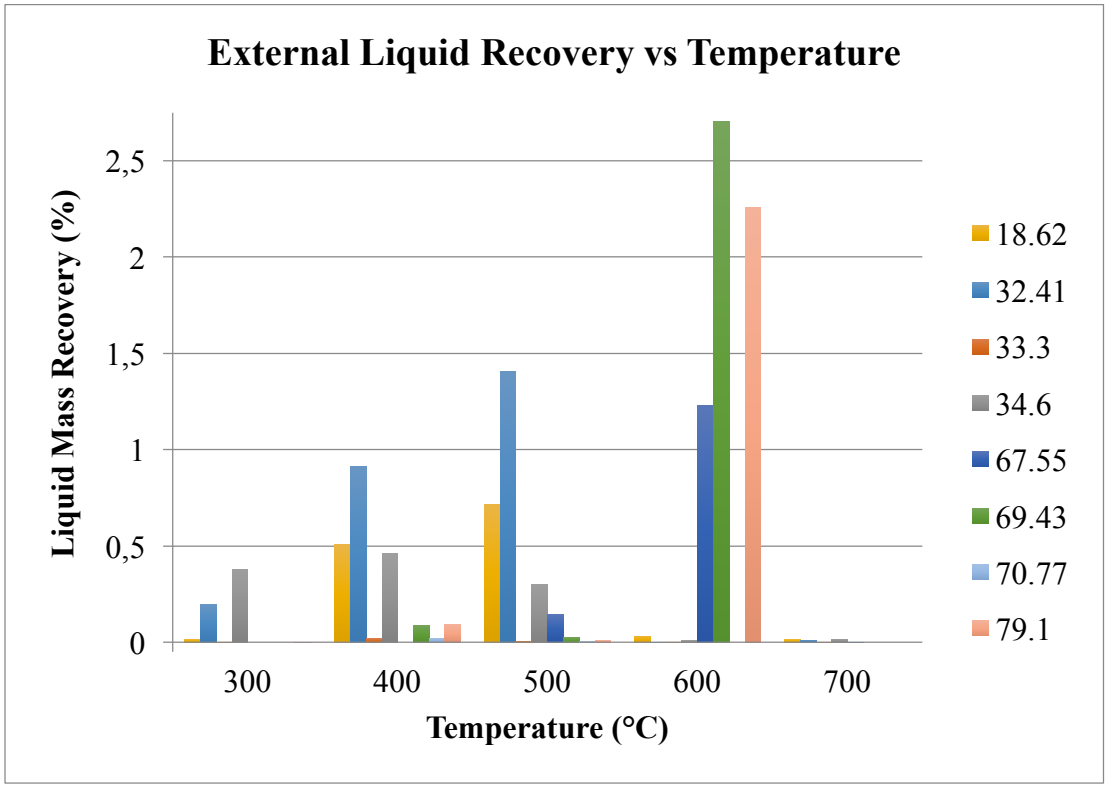


Figure 4.5: External Liquid Recovery at Different Temperatures for Repeat tests using Small Coal Pieces (varying ash content) over a temperature range of 300°C - 700°C

Figure 4.6 shows cumulative external liquid mass recovery. The trends displayed for the small samples are similar to those displayed in Figure 4.2 for the large samples. The graph shows for the lower ash samples the total mass recovered was at lower temperatures, whilst the higher ash content samples (67.55% and above) had volatiles which were extracted at higher temperatures.

The external collection of liquid increases negligibly after reaching a temperature of 500°C, for samples with an ash content in the range 18.6 % - 34.6%. However, for samples with an ash content range 60% - 70%, the mass collected continued to increase until 600°C, after which there is no visible increase. Figure 4.6 shows negligible recovery from some of the high ash samples. It is possible that the organic material was not exposed to the surface and trapped in the interior in these samples (70.77% and 79.1%).

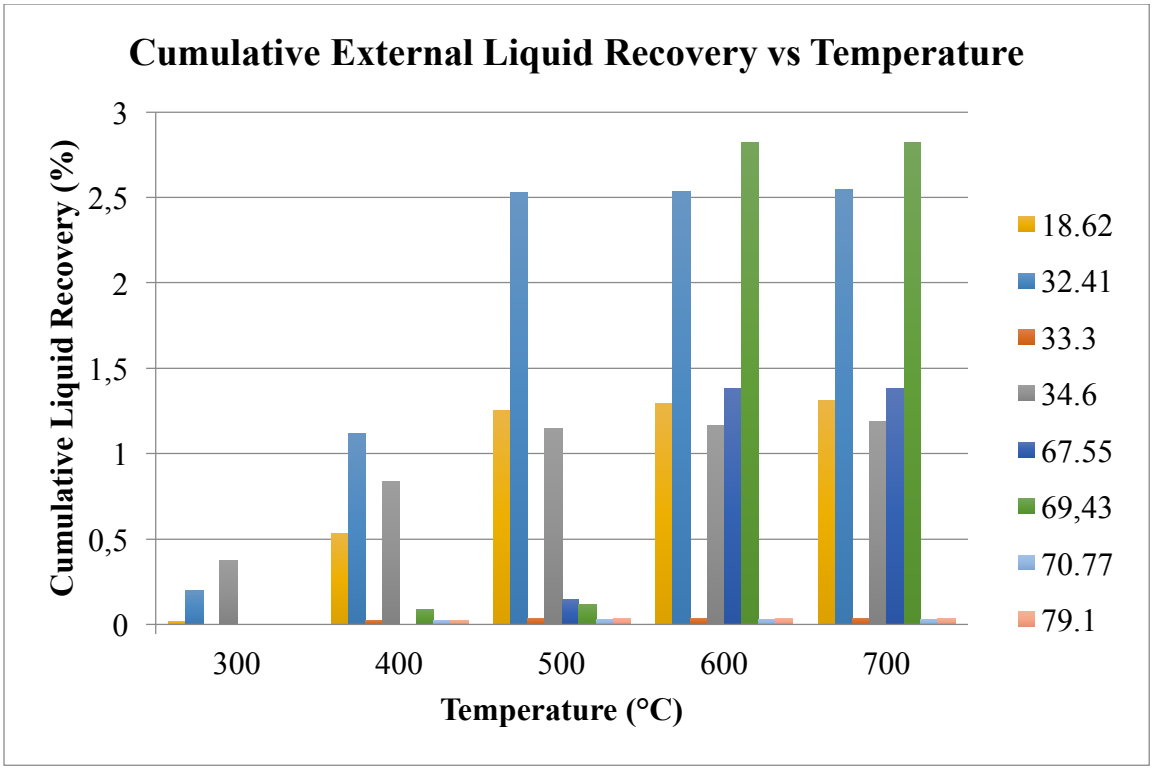


Figure 4.6: Cumulative External Liquid Recovery at Different Temperatures for Repeat tests using Small Coal Pieces (varying ash content) over a temperature range of 300°C - 700°C

Figure 4.7 is generated from the data obtained during the combustion phase of the experiments. This provides the mass of non-volatile material present in each sample.

Figure 4.7 displays similar trends to those seen in Figure 4.3. The gradients shown on the graph in Figure 4.7 also indicate that the greatest mass loss occurs between 400°C - 500°C for the lower ash content (< 40%) samples, but between 500°C - 600°C for the coal samples in the 67.55 % - 79.1 % range.

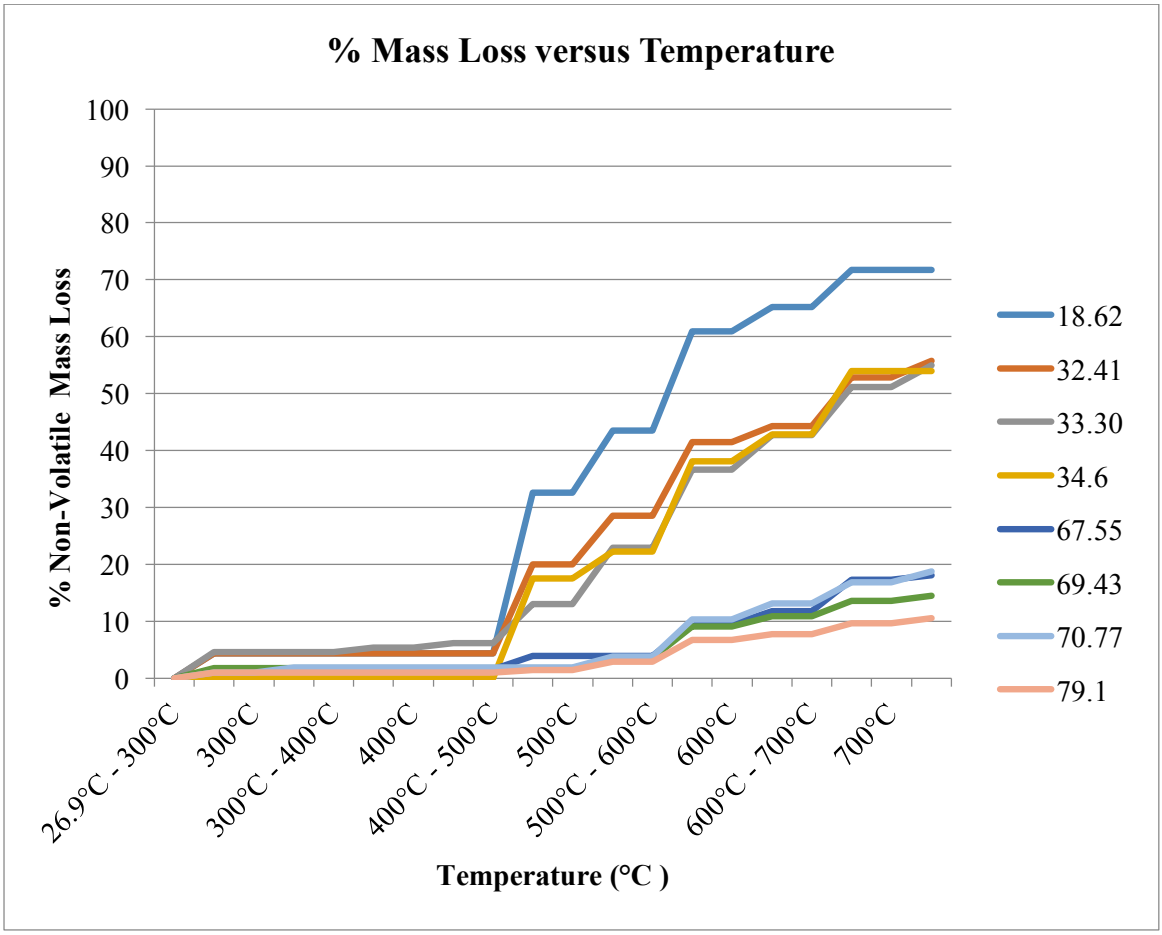


Figure 4.7: Mass Loss during Combustion for Repeat tests using Small Coal Pieces over a temperature range of 27°C - 700°C

On conclusion of the combustion experiments, the spent coal samples were once again examined and revealed that the entire sample was reacted (no unreacted portion was seen). The smaller sized samples were more suitable for use in this laboratory-scale setup as seen in Figure 3.3 in Chapter 3.

4.1.3 Tests at a temperature of 700°C for 1 hour.

The results seen in Figures 4.1 and 4.6 show that volatiles are extracted up to 700°C, however keeping each sample at a particular temperature for 30 minutes may be too long a period of time. In this third set of experiments, the samples were pyrolysed at 700°C for one hour to determine a suitable residence time. A longer residence time implies that a greater amount of energy would be utilized to maintain the temperature. Twelve coal samples were selected by means of the methods described in Chapter 3, with mass ranging from 8.5g to 18.4g. The results follow a similar trend to those obtained in Tables 4.1 and 4.2. An increase in the ash content results in a decreased percent of volatiles and a decrease in the percentage of non-volatile combustibles.

The samples having an ash content above 70% contain a relatively large ratio of volatiles to residual carbon when compared to the samples with an ash content in the range 32% to 37%.

Table 4.3: Overall Summary of Results obtained for Tests at a temperature of 700°C for 1 hour

Initial Sample Mass (g)	% Ash	Volatiles Recovered Externally (Water + Hydrocarbons) (Mass %)	Volatiles Recovered from Reactor & Tubing after the experiment (Mass %)	Non-Volatile Combustibles (Residual Carbon) (Mass %)	% Recovery of Volatiles (Mass Balance Reconciliation)
8.48	**31.70**	6.38	18.92	37.74	98.06
11.88	**32.03**	12.58	11.79	42.10	94.17
11.21	**33.89**	2.92	21.40	41.17	97.51
11.90	**35.54**	4.68	17.65	41.18	95.90
13.62	**37.31**	4.98	19.81	36.70	95.42
9.40	**40.19**	10.74	13.83	35.11	99.46
15.90	**42.26**	11.24	13.21	32.70	97.66
13.78	**46.71**	9.66	11.61	31.21	96.37
12.16	**47.23**	3.4	18.92	28.79	93.14
16.57	**73.01**	3.91	7.24	15.22	94.70
18.37	**82.18**	6.76	5.44	5.44	98.50
13.97	**82.30**	2.42	10.02	5.01	98.01

In this particular set of experiments time was the variable tested. Figure 4.8 shows mass of liquid recovered externally (as per cent mass), with respect to time. The experiment was conducted for one hour with vials containing sample being changed every 15 minutes, and the mass being recorded. After 15 minutes a significant quantity of volatiles was collected for every sample, irrespective of whether the ash content was high or low.

Figure 4.8 also shows that at 30 minutes the vials contained a small quantity of volatiles, however at 45 and 60 minutes the amount collected in the vials was negligible.

It was concluded that a residence time of 30 minutes is sufficient, for conducting the pyrolysis experiments.

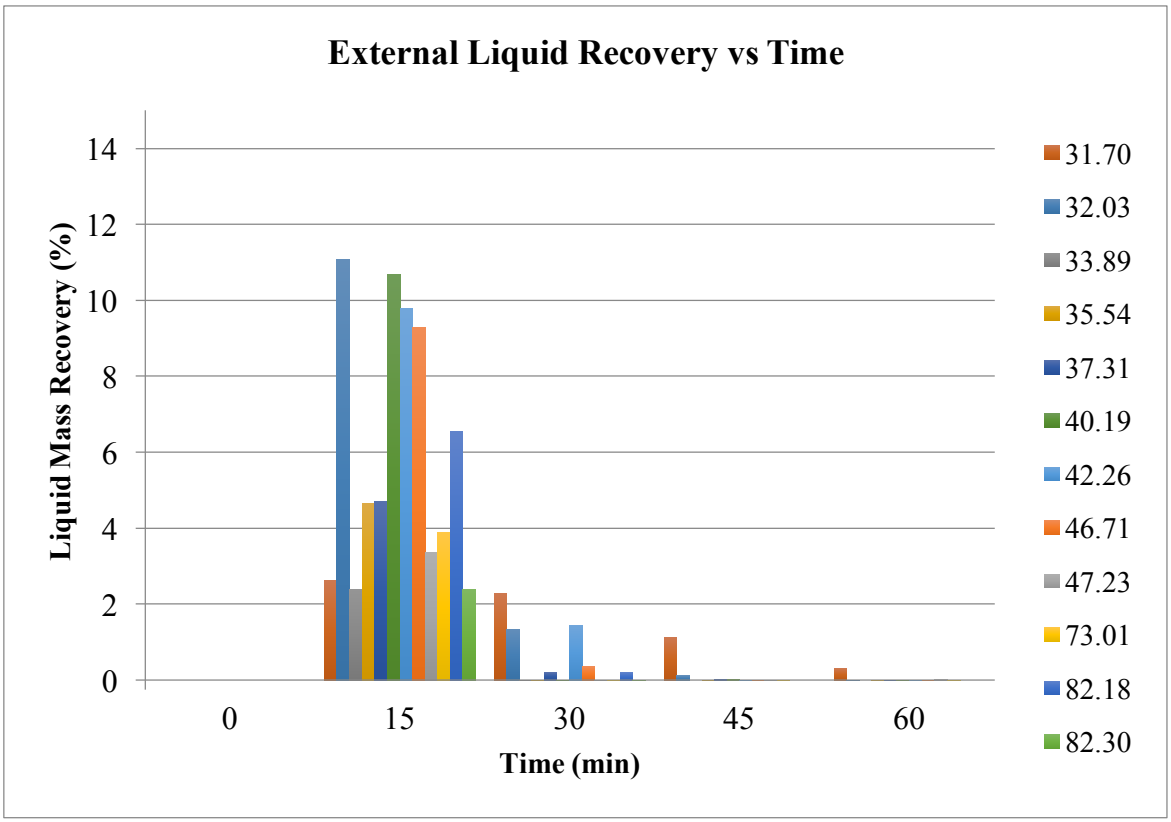


Figure 4.8: External Liquid Recovered during Pyrolysis at Different Time Intervals for Small Coal Pieces at a temperature of 700°C for 1 hour

Figure 4.9 is generated from the data obtained during the combustion phase of the experiments. This provides the mass of non-volatile material present in each sample. Figure 4.9 also displays similar trends to those seen in Figure 4.3 and 4.7. The gradients shown on the graph in Figure 4.9 also indicate that the greatest mass loss occurs between 400°C-500°C for the lower ash content (< 45%) samples but between 500°C-600°C for the coal samples in the higher ash content range.

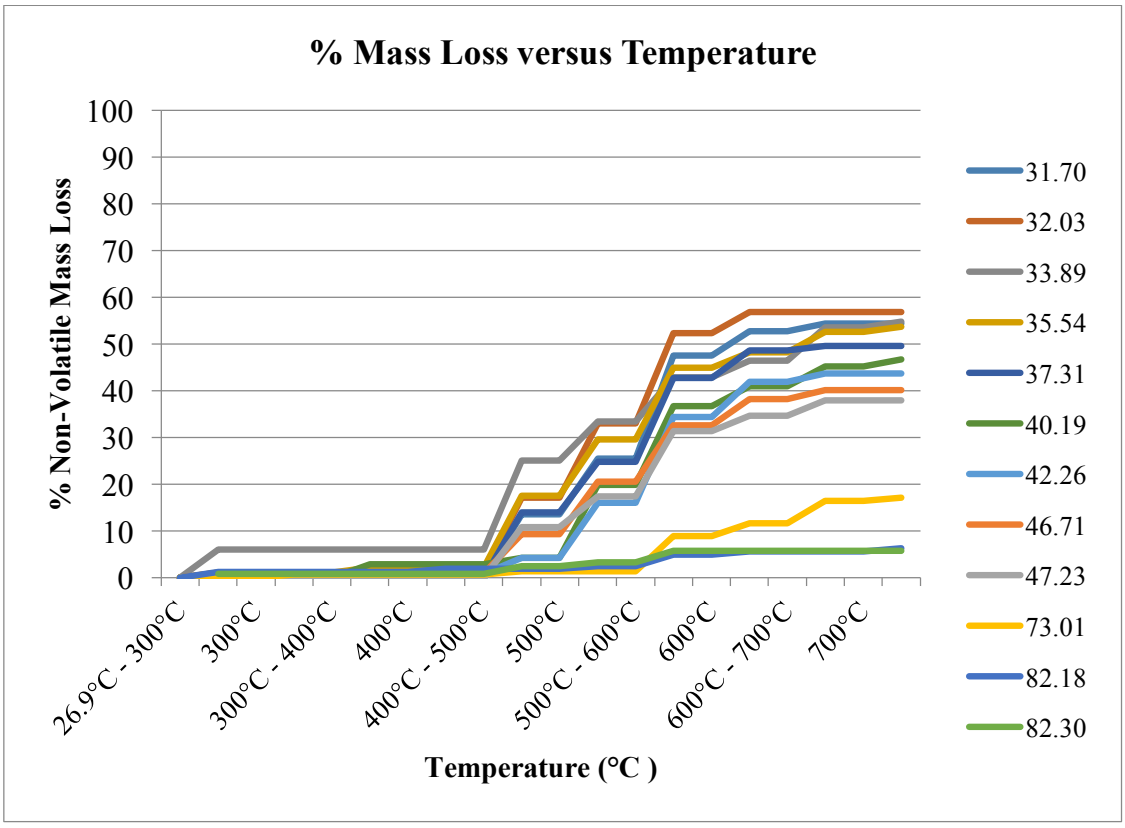


Figure 4.9: Mass Loss during Combustion for tests done for 1 hour

The liquid samples collected externally, and the ethanol solution recovered after washing the reactor and tubing, were sent for analysis by GCMS and Karl Fischer analysis, to determine the composition of the of the volatile matter. However, on subsequent review of the method of sample recovery and dilution, it was concluded that the results were not reliable. Hence these data had to be discarded.

It was therefore decided to perform a final set of tests to confirm the findings and to determine the composition of the volatile material more accurately. The latter will provide an indication of the distribution of the potential products and it will be used for estimating the energy required for pyrolysis.

4.2. Main data set for detailed product analysis (Tests at a temperature of 700°C for 30 minutes.)

The three sets of experiments conducted prior to this have provided useful data to generate this main data set. In the first set of experiments ('large' coal pieces were tested over a temperature range of 300°C - 700°C), it was observed that a small portion of the sample remained unreacted. Hence, for the second set of experiments, smaller coal pieces were tested over a temperature range of 300°C - 700°C), and this size was found to be more suitable for use in the laboratory scale equipment. However, in the first and second experimental sets, the pyrolysis was undertaken for 2,5 hours.

To maintain temperatures for a long period requires more energy, therefore for the third set of experiments (Small Coal pieces at a temperature of 700°C, for a total of 1-hour), time was the variable that was studied.

Utilizing all the prior results, the final set of experiments were conducted at 700°C for 30 minutes. The volatile samples collected were also subjected to GCMS analysis and Karl Fischer analysis. The data provided by the pyrolysis, combustion, GCMS analysis and Karl Fischer analysis was used to generate results in the mass and energy balance circuit.

Table 4.4 displays the same trends as observed in Tables 4.1, 4.2 and 4.3. The ash content of the samples increases whilst the percent volatiles present decreases. Although, the percent volatiles decrease the value still remains high. For example, in the 25.69% ash coal the total volatiles present is 31.55% however in the 65.75% ash coal the total volatiles present is 17.27%. This shows that proportionately the 65.75% ash coal contains significant amounts of volatiles.

Figures 4.1 and 4.5, behave similarly to the mathematically modelled DTG curve of devolatilization (Hattingh, 2012). The graph shows weight loss rate versus temperature. The curve describes coal devolatilisation behaviour as follows (Hattingh, 2012):

- For temperatures from 40°C - 100°C (Hattingh, 2012), there is an initial peak in the weight loss rate, which usually corresponds to the release of moisture/crystalline water.
- Majority of the devolatilisation occurs after 350°C, with the weight loss rate peaking at 500°C and 800°C (Hattingh, 2012).

Table 4.4: Overall Summary of Results for Tests at a temperature of 700°C for 30 minutes

Initial Sample Mass (g)	% Ash	Volatiles Recovered Externally (Water + Hydrocarbons) (Mass %)	Volatiles Recovered from Reactor & Tubing after the experiment (Mass %)	Non-Volatile Combustibles (Residual Carbon) (Mass %)	% Recovery of Volatiles (Mass Balance Reconciliation)
8.56	**25.69**	11.7	19.85	41.05	94.84
8.81	**32.93**	11.23	19.30	34.62	94.07
10.07	**33.75**	10.63	16.88	38.07	97.62
10.10	**35.64**	12.58	13.86	36.07	93.46
11.86	**63.23**	8.13	10.12	18.14	97.94
8.21	**65.75**	13.62	3.65	15.82	93.73

The use of 700°C as a pyrolysis temperature is justified as mathematical modelling shows that maximum weight loss (volatile loss) occurs between 500°C - 800°C (Hattingh, 2012).

The volatiles that were collected externally were composed of a hydrocarbon layer and a small quantity of water at the bottom of the flask. This water layer, may have contained some water-soluble organic compounds, therefore Karl Fischer analysis was used to determine the water content. The results seen in Table 4.5 show that there was very little water present in the samples. This water could have been due to thermal decomposition of some volatile organic compounds. The high ash coals are characterised as having a high water content, however the Karl Fischer analysis shows that coal samples (> 60%) have less than 2% water. Since the water content was low it leaves a relatively high proportion of volatile organic material.

Table 4.4 shows the total amount of volatiles calculated by two methods. The % Volatiles (Water + Hydrocarbons) was calculated by mass loss of the coal sample during pyrolysis. The % Water and % Hydrocarbons amounts were calculated using the actual amount recovered and the Karl Fischer analysis.

Table 4.5: Results obtained after Karl Fischer analysis showing percent Water present in each Sample

% Ash	% Volatiles (Water + Hydrocarbons)	% Water	% Hydrocarbons
25.69	33.26	0.29	31.26
32.93	32.45	1.12	29.41
33.75	28.18	1.09	26.42
35.64	28.29	0.28	26.16
63.23	18.63	1.18	17.07
65.75	18.43	1.84	15.43

Figure 4.10 was generated from the data obtained during the combustion phase of the experiments. This provides the mass of non-volatile material (carbon) present in each sample.

Figure 4.10 displays similar trends to those seen in Figure 4.3 and 4.7. The gradients shown on the graph in Figure 4.9 also indicate that the greatest mass loss occurs between 500°C - 600°C for the lower ash content (< 36%) samples, but not further mass loss occurred above 600°C for the coal samples in the higher ash content range. The O/C decreases and the porosity increases (Odeh et al., 2017)

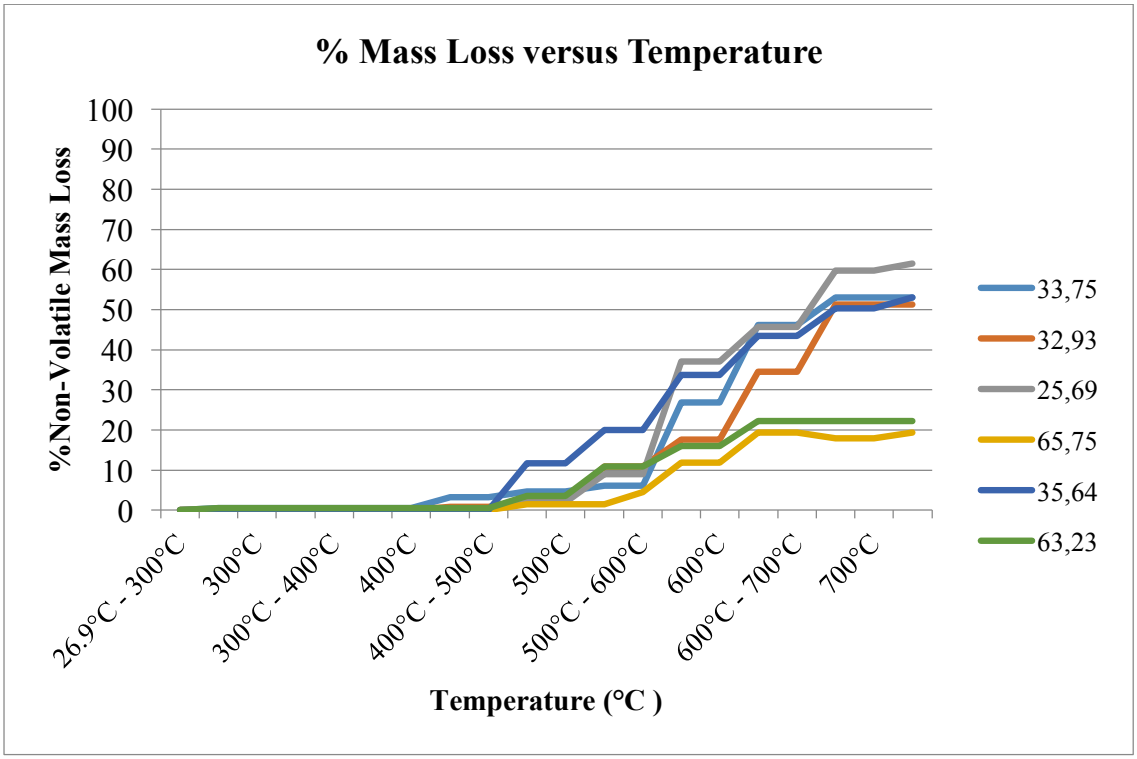


Figure 4.10: Mass Loss during Combustion for tests done for 30 minutes

The samples appearing in Figure 4.11 and 4.12 show the conditions after combustion. The sample in Figure 4.11 has a low ash content (25.69%), this sample did not maintain its structure. It disintegrated into dust which is problematic for use in a reactor, as discussed in Chapter 3.

Figure 4.11: Low Ash (25.69%) content coal sample disintegrating into dust

Figure 4.12 has a high ash content 63.23%. The high ash content samples maintain their shape, which makes then more suitable for use in the proposed reactor design.

Figure 4.12: High Ash (63.23%) content coal maintaining original structure

The layered structure suggests that the coal pyrolysis and combustion may have been facilitated by the presence of bands of coal with a relatively low ash content. Hence, the model for diffusion through a uniform layer of ash would not apply. The data is unfortunately not suitable for testing the model, as a large proportion of the volatile material condensed inside the reactor and exit tube.

4.2.1 GCMS Analysis of the Samples of Volatile Material

Appendix B lists some of the many organic compounds which were positively identified by GCMS analysis. In order to simplify the analysis, all the organic compounds, which were positively identified, were classified in terms of boiling point. The guideline for classification of crude oil into boiling point ranges was obtained from the T0KToL website. The distribution by mass organic compounds is shown in Table 4.6, classified into: Light Oil (30°C - 180°C), Heavy Oil (181°C - 300°C) Tar (> 300°C) and Unidentified Compounds.

Table 4.6: Mass distribution of Organic Compounds recovered from Inside the Reactor and Exit tube

		Ash Content (%)					
	Boiling Point Range (℃)	**25.69**	**32.93**	**33.75**	**35.64**	**63.23**	**65.75**
Light Oil	**30 -180**	34.96	57.03	25.14	37.8	36.81	31.43
Heavy Oil	**181 - 300**	47.21	26.06	57.5	54.54	47.97	47.98
Tar	**> 300**	2.01	5.44	2.51	3.35	4.56	11.86
Unidentified	**Unknown**	15.82	11.55	14.55	4.31	10.66	8.73

Table 4.7: Mass distribution (%) of Organic Compounds in the of Organic Fraction, recovered Externally

		Ash Content (%)					
	Boiling Point Range (℃)	**25.69**	**32.93**	**33.75**	**35.64**	**63.23**	**65.75**
Light Oil	**30 -180**	24.65	0	35.26	1.98	4.07	36.11
Heavy Oil	**181 - 300**	48.52	84.41	60.69	77.77	85.46	38.51
Tar	**> 300**	0	10.24	2.93	10.17	6.75	2.59
Unidentified	**Unknown**	26.83	5.35	1.12	10.08	3.72	22.79

Table 4.8: Mass distribution (%) of Organic compounds in the Aqueous Fraction, recovered Externally

		Ash Content (%)					
	Boiling Point Range (℃)	**25.69**	**32.93**	**33.75**	**35.64**	**63.23**	**65.75**
Light Oil	**30 -180**	9,56	22,08	0	7,58	8,71	17,32
Heavy Oil	**181 - 300**	19,17	60,5	0	86,88	87,05	75,61
Tar	**> 300**	0	0	0	0	1,05	0
Unidentified	**Unknown**	71.27	17.42	0	5.54	3.19	7.07

The mass of organic compounds recovered via the external collection (Organic and Aqueous), and internal collection, were combined to yield the total mass of each type of compound recovered.

Table 4.9 shows the top five highest mass compounds found in each coal sample. The results are similar for each of the different ash content samples as they have common compounds occurring. The data shows that phenols appear in relatively large quantities, which is problematic for further processing and blending with crude oil. The phenols are also a major industrial product which can be separated from oil by means of solvent extraction.

Table 4.9: Top 5 Highest Percent Compounds found in each Sample

Ash Content (%)	**25.69**	**32.93**	**33.75**	**35.64**	**63.23**	**65.75**
Components	Propane, 1-(1-ethoxyethoxy)-	Propane, 1,1-diethoxy-	Pyridine, 2,4-dimethyl-	Phenol, 2-methyl-	Benzene, 1,3-dimethyl-	Pyridine, 2,3,6-trimethyl-
	Decane	Cyclohexane, (2-methylpropyl)-	Propane, 1,1-diethoxy-	Propane, 1-(1-ethoxyethoxy)-	Naphthalene, 2-methyl-	Phenol, 2,6-dimethyl-
	Phenol	Phenol, 2-methyl-	Undecane	Phenol, 2-methyl-	Phenol, 2-methyl-	Benzene, 1,2,3-trimethyl-
	Undecane	Phenol	Phenol, 2-ethyl-	Phenol, 2,6-dimethyl-	Phenol	Pyridine, 3-methyl-
	Phenol, 2-methyl-	Decane	.alpha.-Terpineol	.alpha.-Terpineol	Phenol, 3-ethyl-	Phenol, 3-ethyl-

Chapter 5

Concept and Design of Chemical Extraction Unit, Mass and Energy Balance

5.1 Concept and Design of an Industrial Chemical Extraction Unit

5.1.1 Process Description

Figure 5.1 shows the initial concept and design of an industrial scale reactor, for extraction of volatiles (hydrocarbons) by pyrolysis, and to combust the char, to provide the energy to run the process. This design was conceptualized by Prof. B.K.Loveday (personal communication, March, 2013).

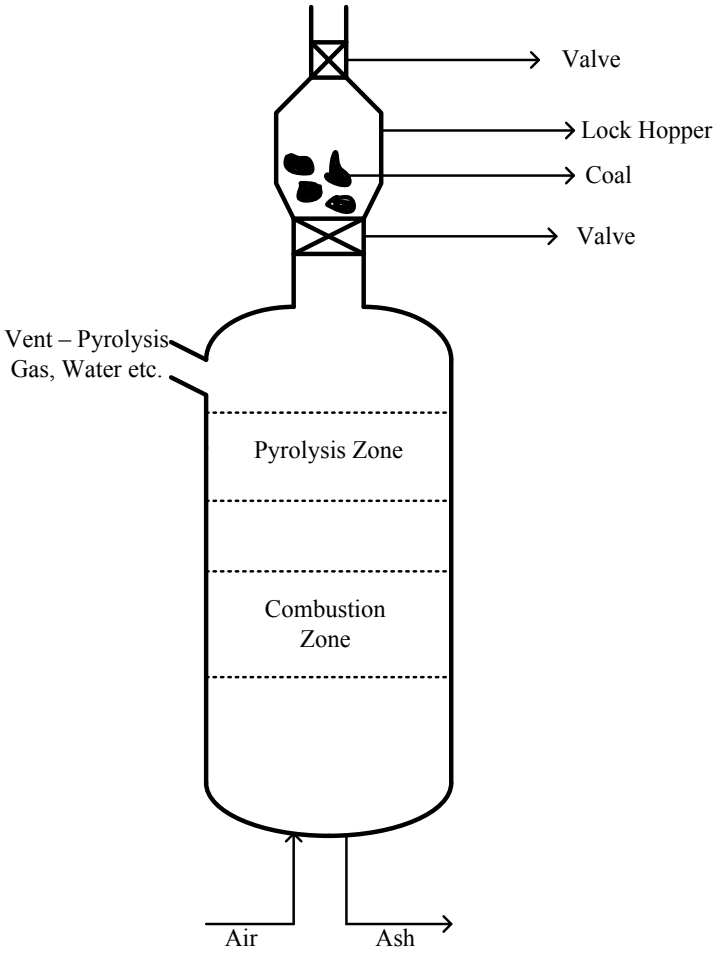


Figure 5.1: Design of Industrial Counter-current Reactor for Pyrolysis and Combustion of Coal

For the purposes of this investigation, coal was characterized as follows:

- Carbon
- Water
- Hydrocarbons
- Ash (all remaining material after combustion)

Pyrolysis

As explained in the introduction, the feed consisted of coal with a high ash content (about 50%) from the Waterberg coalfield. It will enter a lock hopper under gravity, via a control valve. The purpose of the lock hopper is to prevent air from entering the system. (Some air will be entrained, but the mass will be a small). Once the first valve is closed, the lower valve will be opened periodically to allow the coal to gravitate into the pyrolysis zone.

The solids in the reactor move down the reactor due to gravity. The flow is controlled at the bottom exit by, for example, a screw conveyor. As the coal moves down into the pyrolysis zone, it is heated by the counter-current flow of hot gases from the combustion zone and pyrolysis occurs, thereby removing the volatiles (water and volatile organic compounds) as gases. This gaseous product stream leaves the reactor via a vent situated at the top of the column.

The inert material in Waterberg coal is often intimately mixed with the organic material and hence it is envisaged that the rate of pyrolysis will become dependent on diffusion through the porous layer of char, as the core of unreacted coal shrinks (Sinnott, 2005). The rate of the pyrolysis reaction, particularly that of the larger particles, will be influenced by particle size and temperature.

Combustion

Combustion of the carbon in the char provides the energy necessary to drive the process. The char enters the combustion zone, where the carbon reacts with air. It is envisaged that the flow of air will be controlled, so that the oxygen (limiting) is fully consumed in the combustion zone. The hot gases leaving the combustion zone (N_2, CO and CO_2) do not react with the volatile organic compounds in the pyrolysis zone. The rate of combustion will therefore also be dependent on temperature (Toporov, 2014) and particle size. The ash can then be discarded.

Introduction of Air

Air is essential to drive the combustion reactions. Prior to entering the combustion zone the air needs to be pre-heated. Heat exchange can be used with the exit gases, which require cooling for recovery of the volatiles. Lastly, the air is brought to a final temperature by heat exchange with hot ash leaving the combustion zone.

Particle Size

The coal delivered from mining is normally crushed to a top size suitable size for further processing (e.g. upgrading via heavy medium separation). The envisaged process requires counter-current flow of gas and solids, for heat exchange, and hence the particles must be large enough to allow the air required for combusting the char, to flow through the bed. There will be a distribution of particle sizes and it may be necessary to remove the very fine coal particles from the feed, to ensure free flow of gas. It also means that the particles should ideally retain their original size when they are transformed into ash, and not disintegrate into fine powder, as this will cause the lower portion of the reactor to block or form channels. This is a critical requirement of the process.

Upgrading of the Valuable Product (Hydrocarbons)

The gaseous stream leaving the reactor via the vent will contain hydrocarbons (valuable product), water and combustion gases. The stream is upgraded using a series of heat exchangers and separators to eventually collect the valuable pyrolysis liquids. The pyrolysis liquid will have to be upgraded by means of distillation and other processes.

Disposal of Residual gas

It is envisaged that the gas stream leaving the system could be flared (after mixing it with air), to burn the carbon monoxide, and other combustible gases,

5.2 Mass and Energy Balance

A very important aspect of this dissertation is the calculation of the mass and energy balance for the circuit, as seen in Figure 5.2. The experimental data obtained for the various coal samples was used to calculate the mass and energy balance and hence to determine the feasibility of this project.

The calculations were done using the results obtained in Chapter 4. For the mass balance portion the flowrates were determined using the mass fractions calculated in Chapter 4. Since a series of heat exchangers were used, the following equation from (Incopera et. al, 2007) was used:

$$Q = mCp\Delta T \tag{5.1}$$

The equation was manipulated to calculate the required stream temperatures, whilst the Cp values were determined from the GCMS results in Appendix B. The amount of energy available was determined by calculated the heat of reaction, which can be seen in Appendix C-1.

5.2.1 Mass and Energy Balance Circuit Design

Figure 5.2 shows an in-depth view of the mass and energy balance circuit. The mass and energy balance circuit was designed to extract the hydrocarbons (saleable product) as well as effectively utilise the energy released within the system to run this process.

The circuit is made up of a reactor (made up of 3 zones), a series of heat exchangers as well as gas-liquid separators. The temperatures below refer to average temperatures. For the purposes of the calculations, the zones are assumed to be perfectly mixed. Preliminary mass and energy balances highlighted where excess energy was available. For calculation purposes heat losses were not taken into account, as the heat loss is a function of the heat exchanger and reactor sizes, the lagging used, etc. Key temperatures, such as the combustion and pyrolysis temperatures, were chosen on the basis of laboratory data. The combustion temperature had to be about 200°C higher than the pyrolysis temperature to achieve an energy balance.

Reactor

The reactor is a single unit which comprises of 3 parts, namely, a Pyrolysis Zone, a Combustion Zone and a Heat Exchange Zone. It was assumed that the relatively high-ash particles would maintain its shape and allow the gas to flow upward, counter-current to the flow of solids.

Pyrolysis Zone

The coal samples, which are composed of carbon, hydrocarbons, inert material (reported as the ash content) and water, enter this zone first via Stream 1. The pyrolysis zone was set to operate at a temperature determined by the results of mass recovery at various temperatures. The pyrolysis experiments were conducted at a temperature of 700°C to maximise volatile recovery. Figure 4.5, as well as the GCMS analysis seen in Appendix B, indicate that a temperature of about 600°C was adequate for recovery of the more volatile components with a residence time of half an hour. It was therefore decided that the mass and energy balance calculation should be assessed using 600°C as the pyrolysis temperature. This zone is devoid of any air which therefore allows for the coal to be heated up sufficiently to allow for the release of the volatiles (hydrocarbons and water), which are extracted via Stream 4. The energy required for the devolatilisation of the coal sample is provided by cooling the hot gases from the combustion zone. The residual carbon in the coal (char), after removal of the volatiles (hydrocarbons + water), leaves via Stream 2.

Combustion Zone

Stream 2, which contains residual carbon and ash (char), now enters the combustion zone which was set to operate at a fixed temperature. In view of the choice of 600°C as the pyrolysis temperature, a combustion temperature of 800°C was chosen. The char is brought into contact with preheated air from Stream 6, which reacts with the carbon. An exothermic reaction occurs which gives off energy, which sustains the combustion at the selected temperature. The flow of air entering the combustion zone must be controlled so that it remains as the limiting agent. No excess oxygen should be present as it would rise up into the pyrolysis zone and combust the hydrocarbons released within the pyrolysis zone.

Preheating Air

The temperatures of streams leaving the heat exchangers were set in some cases to maintain a 20°C difference where applicable.

Heat Exchanger 1

Ambient air (nitrogen and oxygen) enters the system via Stream 13, where it undergoes the first pre-heating stage, by exchange with the heat given off by the waste gas stream, which contains water (steam), nitrogen, carbon dioxide and carbon monoxide.

Heat Exchanger 2

The warm air enters heat exchanger 2 via Stream 9 where it undergoes the second pre-heating stage of heating by exchange with the heat given off by cooling Stream 4 which contains the hydrocarbons and waste gas. The cooling of Stream 4 serves a dual purpose by heating up the incoming air in Stream 9, as well as allowing for the separation of the potentially valuable product from the waste gas.

Heat Exchanger 3

Lastly, the air (Stream 7) was heated utilising the hot waste ash leaving the combustion zone. The pre-heated air then enters the combustion zone to react with the carbon.

Gas-liquid Separators

Also contained within this mass and energy balance circuit are two gas-liquid separators. Separator 1, serves to split the hydrocarbons (product) from the waste gas. Stream 11 enters Separator 1 and is split into Stream 17 (containing the hydrocarbons) and Stream 12 which contains the waste gas. Some condensation of water will occur in Heat Exchanger 1 and Separator 2 provides for separation of this water and possibly some remaining hydrocarbons.

Water Cooling

Cooling water is used in Stream 18 to cool down the hydrocarbons so that the liquid hydrocarbons could be separated from the waste gases in Separator 1. The water which was converted into steam (Stream 19) can be utilised as an external heat source to help maintain the reactor operating temperature since heat losses were not taken into account.

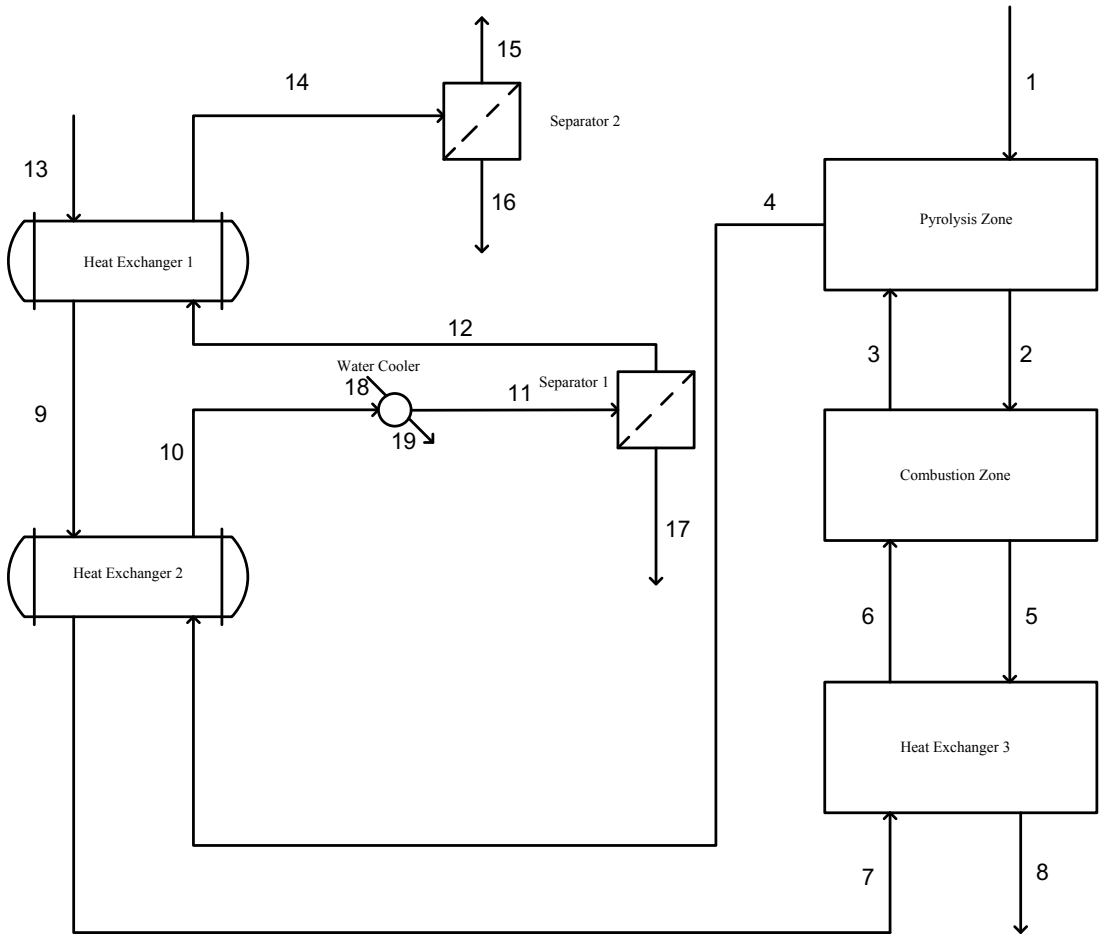


Figure 5.2: Mass and Energy Balance Circuit Design

5.3 Mass and Energy Balances for Pyrolysis at 600°C

The volatile material recovered from the samples varied in mass and composition. Hence, a separate mass and energy balance was calculated for each sample reported in Chapter 4, using 'small' coal pieces.

Calculations were done for four low ash content samples (25.69% - 35.64%) and two high ash content samples (63.23% and 65.75%). The differences between the results obtained for the energy balances are highlighted below. The following liquid samples collected were separated into the following categories: Organic Compounds recovered from Inside the Reactor and Exit tube, Organic Compounds in the Organic Fraction, recovered Externally and Organic compounds in the Aqueous Fraction, recovered Externally. For the figures below the samples are referred to as Inside, Top and Bottom respectively.

5.3.1 Mass and Energy Balance for a Low Ash Sample (35.6%)

Figure 5.3 shows the mass balance circuit for 35.6 % ash content coal. A basis of 100 kg/hr of coal entering was chosen for Stream 1, which enters the pyrolysis zone of the reactor. The results shown in Table 4.4 provided the percentages for the amount of carbon and ash present in Stream 1. The Karl Fischer analysis results shown in Table 4.5 provides an indication of the percentage water present in each sample which then could be subtracted from the volatiles percentage to given the percent hydrocarbon present. Stream 1, entering at room temperature was set at $T_1 = 25°C$.

The temperature of the pyrolysis zone was set at 600°C, this was chosen based upon the results shown by Figure 4.5. The boiling points of the hydrocarbon compounds were found in literature. The highest boiling point of 358.8°C (Chemspider, 2016) was exhibited by the compound 9,10-Dimethylanthracene as shown in Appendix B. In the pyrolysis zone the hydrocarbons and water are released from the coal sample leaving behind carbon and ash which exit via Stream 2 at $T_2 = 600°C$ to enter the combustion zone. Stream 3 which contains the combustion reaction by-products (carbon dioxide and carbon monoxide) and nitrogen from the air, also enters the pyrolysis zone with $T_3 = 800°C$. Stream 4 which exits the pyrolysis zone at 600°C, contains the hydrocarbons, water and combustion waste gases.

A temperature of 800°C was selected for the combustion zone. Stream 2, which contains carbon and ash enters the combustion zone at 600°C. The flowrate of carbon is 36.07 kg/hr. The carbon from Stream 2 reacts with the oxygen from the preheated air which enters via Stream 6 with $T_6 = 595.56°C$ to produce carbon dioxide and carbon monoxide as reaction by-products. The carbon dioxide and carbon monoxide are produced in a 1:1 ratio as shown indicated by the Ellingham diagram in Appendix E for an operating temperature of 700°C however, this ratio can be maintained by adjusting the partial pressure of oxygen. The nitrogen gas present in the air also exits with the reaction by-products via Stream 3. The remaining ash then exits the combustion zone with $T_5 = 800°C$.

It should be noted that the calculation of the energy balances in the combustion zone and pyrolysis zone were based on a simplifying assumption of perfect mixing. The temperature of the streams leaving the combustion zone was therefore pre-defined at 800°C. The energy balance can be calculated, as shown in Appendix C and the result indicates that an excess of energy is available. The method is conservative, as the exiting streams could leave at a lower temperature.

A very important aspect was utilising the energy available in the system to heat up the air entering the system via Stream 13 at T_{13} = 25°C. Heat exchange between the hot exiting gas and the incoming air was used, as practiced in coal fired power stations. The energy balance calculations assumed counter-current flow of the gases and a difference of 20°C or more, where applicable.

In Heat Exchanger 1, the air undergoes the first stage of pre-heating, utilising the hot gases leaving the system (nitrogen, carbon monoxide, carbon dioxide and steam). Stream 12, which is set at a temperature 120°C (to ensure that water is excluded from Stream 17, the crude hydrocarbon product stream) is cooled to 50°C. This heats the air which leaves via Stream 9 up to a temperature of 98.82°C. Stream 14, then flows into a gas-liquid separator to separate the water from the gases. Streams, 15 and 16 need further treatment before they are released into the environment. Stream 15, which contains the nitrogen and reaction by-products (carbon dioxide and carbon monoxide) could undergo gas scrubbing or it could be flared before it is released. Stream 16 is mainly water, and it needs to be processed, to ensure that the stream conforms with environmental regulations, as it contains some water-soluble compounds. This processing could include the use of bacteria to consume the organic compounds and convert them into carbon dioxide.

The second stage of air pre-heating takes place in heat exchanger 2, where Stream 4 which contains the hydrocarbons (which are divided into 3 portions as described in Chapter 3), nitrogen, carbon dioxide, carbon monoxide and water, is cooled. Stream 4, which leaves the pyrolysis zone at T_4 = 600°C is cooled to 224°C. The air which enters at 98.8°C exits via Stream 7 at a temperature of 580°C. Stream 10 is cooled to 120°C in another heat exchanger, by using water to raise steam at 110°C. Stream 18, contains 19.1 kg/hr of water which is converted into steam. This steam could be utilised to help maintaining the reactor operating temperature. (Heat losses were not taken into account as it is dependent on the size and area of the equipment.) Stream 11 enters gas-liquid separator which separates the hydrocarbons from the nitrogen, carbon dioxide, carbon monoxide and water. The hydrocarbons (valuable product) which leave the system via Stream 17, will then undergo distillation and further refining to grade and sort the compounds. (Beyond the scope of this assignment)

The last stage of preheating occurs in heat exchanger 3 where the air is preheated by cooling the ash. The air enters via Stream 7 at 580°C and is heated to 596°C in Stream 6. The ash is cooled from 800°C in Stream 5 when it exits the combustion zone to 600°C in Stream 8.

However, it should be noted in Figure 4.11, this low-ash sample disintegrates into powder, which makes it unsuitable for use in this process as the heat exchanger would block under the weight of material above, and not allow the air to flow.

Mass and energy balances, which appear in Appendix D, were done for three more low ash samples ranging in from (25.69% - 33.75%). The results obtained follow the same trends as seen for the 35.64% sample.

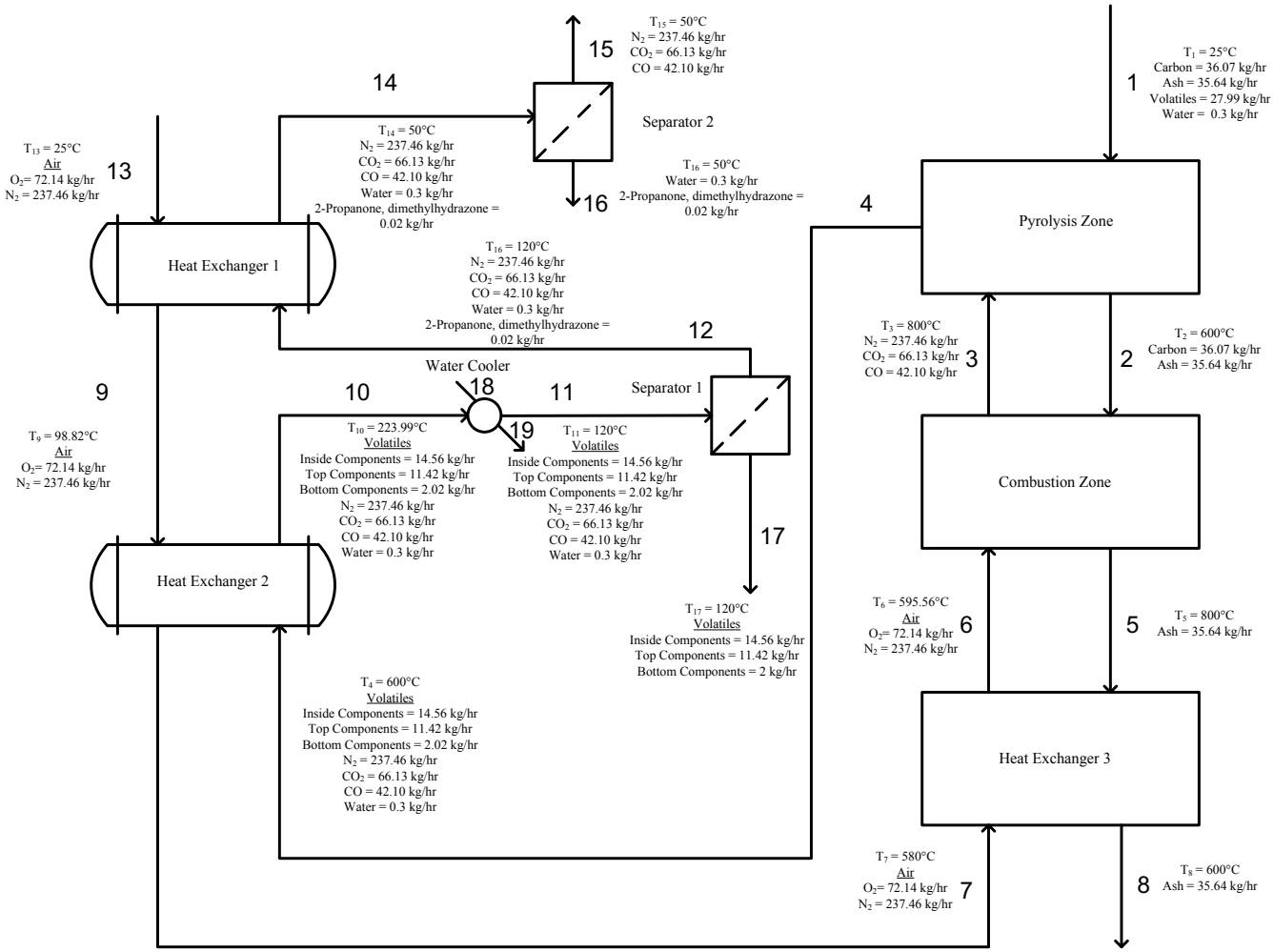


Figure 5.3: Mass and Energy Balance Circuit for Low Ash Coal Sample (35.6%)

Table 5.1: Showing the Stream Properties for 35.6% Ash Content Coal

	Stream																
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
Temperature (ºC)	25	600	800	600	800	595.56	580	600	98.82	223.99	120	120	25	50	50	50	120
Components (kg/hr)																	
Carbon	36.07	36.07															
Ash	35.64	35.64			35.64			35.64									
Volatiles	27.99																
Inside Components				14.56						14.56	14.56						14.56
Top Components				11.42						11.42	11.42						11.42
Bottom Components				2.02						2.02	2.02						2.02
Water	0.3			0.3						0.3	0.3	0.3		0.3		0.3	
N_2			237.46	237.46		237.46	237.46		237.46	237.46	237.46	237.46	237.46	237.46	237.46		
CO_2			66.13	66.13						66.13	66.13	66.13		66.13	66.13		
CO			42.10	42.10						42.10	42.10	42.10		42.10	42.10		
O_2						72.14	72.14		72.14				72.14				
2-Propanone,dimethylhydrazone												0.02		0.02		0.02	

5.3.2 Mass and Energy Balance for a High Ash Sample (63.23%)

Figure 5.4 shows the results obtained for 63.23% ash content coal, which is a high ash coal. This was viewed as a real test of the concept, as counter-current heat exchange would be essential, because of the reduced amount of carbon in the char and the larger proportion of ash, which needs to be brought up to reaction temperature. A basis of 100 kg/hr of feed was selected and the following results were obtained.

The GCMS results indicated that the highest boiling substance was Thymine with a boiling point of 366.8°C. The pyrolysis zone was set at 600°C in order to release the hydrocarbons as indicated by Figure 4.5, which shows that for high ash samples the hydrocarbons are released at higher temperatures. The hydrocarbon flowrate was 17.43 kg/hr. The amount of hydrocarbons released was higher than expected, when compared to the low ash sample (25.69%), which has a hydrocarbons flowrate of 32.96 kg/hr. The char (carbon and ash) leaves the pyrolysis zone via Stream 2 at T_2 = 600°C to enter the combustion zone. Stream 3, which contains the combustion reaction by-products (carbon dioxide and carbon monoxide) and nitrogen from the air also enters the pyrolysis zone with T_3 = 800°C. Stream 4, which exits the pyrolysis zone at 600°C contains the hydrocarbons, water and combustion waste gases.

A temperature of 800°C was selected for the combustion zone, as it has to be significantly higher than the pyrolysis zone temperature and the rate of combustion increases significantly with temperature. Figure 4.10 shows that most of the reaction occurs after 600°C for the high ash content samples. Stream 2, which contains carbon and ash enters the combustion zone at 600°C. The flowrate of carbon is 18.14 kg/hr and this reacts with 36.28 kg/hr of oxygen, which was calculated using reaction stoichiometry as shown by the sample calculations in Appendix C. The carbon from Stream 2 reacts with the oxygen from the preheated air which enters via Stream 6 with T_6 = 634.90°C to produce carbon dioxide and carbon monoxide as reaction by-products.

The air undergoes preheating as described for Figure 5.3. In Heat Exchanger 1, the air is heated up to a temperature of 100.4°C which leaves via Stream 9. The second stage of air pre-heating takes place in heat exchanger 2, where Stream 4, which contains the hydrocarbons, is cooled from 600°C to 252.7°C. The air which enters at 100.4°C, exits via Stream 7 at a temperature of 580°C. Cooling water with a flowrate of 14.04 kg/hr was required to cool and liquefy the valuable hydrocarbons so that it could be extracted from the waste gases and water.

The last stage of preheating occurs in Heat Exchanger 3 where the air is preheated by cooling the ash. The air enters via Stream 7 at 580°C and is heated to 634.9°C in Stream 6. The air is pre-heated to a significantly higher temperature, when compared to a low ash sample since less oxygen is required to react with a smaller amount of carbon and there is a large amount of ash present in the system. The ash is cooled from 800°C in Stream 5 when it exits the combustion zone to 600°C in Stream 8. The ash sample after combustion and heat exchange remains as whole pieces as seen in Figure 4.12 which are more suited for the proposed process.

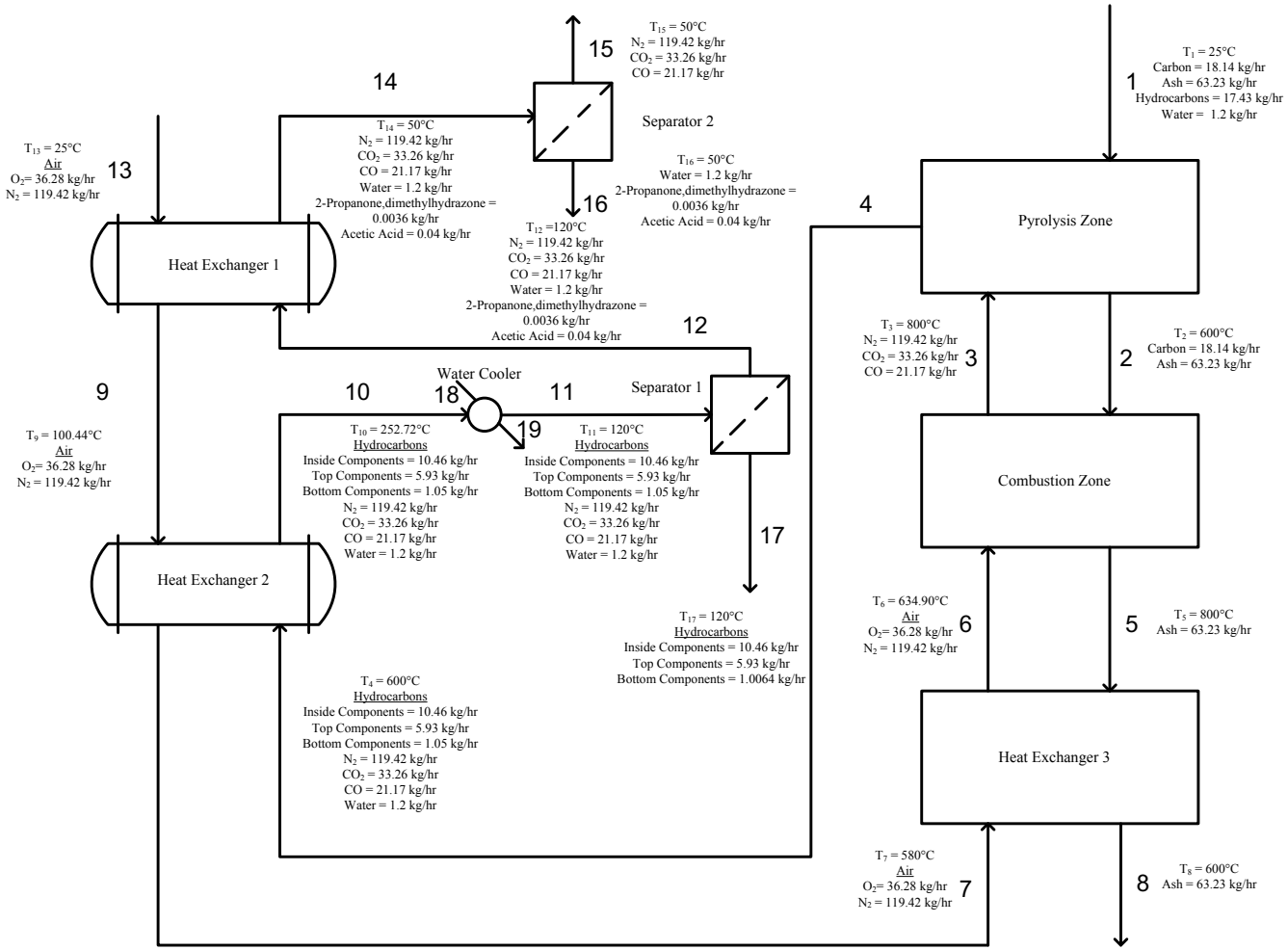


Figure 5.4: Mass and Energy Balance Circuit for High Ash Coal Sample (63.23%)

Table 5.2: Showing the Stream Properties for 63.23% Ash Content Coal

	Stream																
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
Temperature (°C)	25	600	800	600	800	634.9	580	600	100.44	252.72	120	120	25	50	50	50	120
Components (kg/hr)																	
Carbon	18.14	18.14															
Ash	63.23	63.23			63.23			63.23									
Volatiles	17.43																
Inside Components				10.46						10.46	10.46						10.46
Top Components				5.93						5.93	5.93						5.93
Bottom Components				1.05						1.05	1.05						1.0064
Water	1.2			1.2						1.2	1.2	1.2		1.2		1.2	
N2			119.42	119.42		119.42	119.42		119.42	119.42	119.42	119.42	119.42	119.42	119.42		
CO2			33.26	33.26						33.26	33.26	33.26		33.26	33.26		
CO			21.17	21.17						21.17	21.17	21.17		21.17	21.17		
O2						36.28	36.28		36.28				36.28				
2-Propanone,dimethylhydrazone												0.0036		0.0036		0.0036	
Acetic Acid												0.04		0.04		0.04	

5.3.3 Mass and Energy Balance for a High Ash Sample (65.75%)

Figure 5.5 shows the results obtained for 65.75% ash content coal. The GCMS results indicated that the highest boiling substance was 9H-Fluoren-9-ol with a boiling point of 356.6°C, therefore the pyrolysis zone was set at 600°C in order to release the hydrocarbons. The amount of hydrocarbons released is 16.46 kg/hr which is high especially for an ash content of 65.75%. The carbon and ash which exit the pyrolysis zone, via Stream 2 at T_2 = 600°C to enter the combustion zone. Stream 3 which contains the combustion reaction by-products (carbon dioxide and carbon monoxide) and nitrogen from the air also enter the pyrolysis zone with T_3 = 800°C. Stream 4 which exits the pyrolysis zone at 600°C, contains the hydrocarbons, water and combustion waste gases.

The temperature in the combustion zone was set at 800°C, as with the other mass and energy balances , because Figure 4.10 shows that most of the reaction occurs after 600°C for the high ash content samples. Stream 2, which contains carbon and ash enters the combustion zone at 360°C. The flowrate of carbon is 15.82 kg/hr and this reacts with 31.64 kg/hr of oxygen, which was calculated using reaction stoichiometry as shown by the sample calculations in Appendix C. The carbon from Stream 2 reacts with the oxygen from the preheated air which enters via Stream 6 with T_6 = 645.46°C to produce carbon dioxide and carbon monoxide as reaction by-products.

The air undergoes preheating as described for Figures 5.3 and 5.4. In heat exchanger 1, the air is heated up to a temperature of 102.51°C which leaves via Stream 9. The second stage of air pre-heating takes place in heat exchanger 2, where Stream 4 which contains the hydrocarbons is cooled from 600°C to 256.43°C. The air which enters at 102.51°C, exits via Stream 7 at a temperature of 580°C.

The last stage of preheating occurs in heat exchanger 3 where the air is preheated by cooling the ash. The air enters via Stream 7 at 580°C and is heated to 645.46°C in Stream 6. The air is pre-heated to a significantly higher temperature since lesser oxygen is required to react with a smaller amount of carbon and a there is a large amount of ash present in the system. The ash is cooled from 800°C in Stream 5 when it exits the combustion zone to 600°C in Stream 8. The ash sample after combustion and heat exchange remains as whole chunks which makes it suitable for use in this circuit.

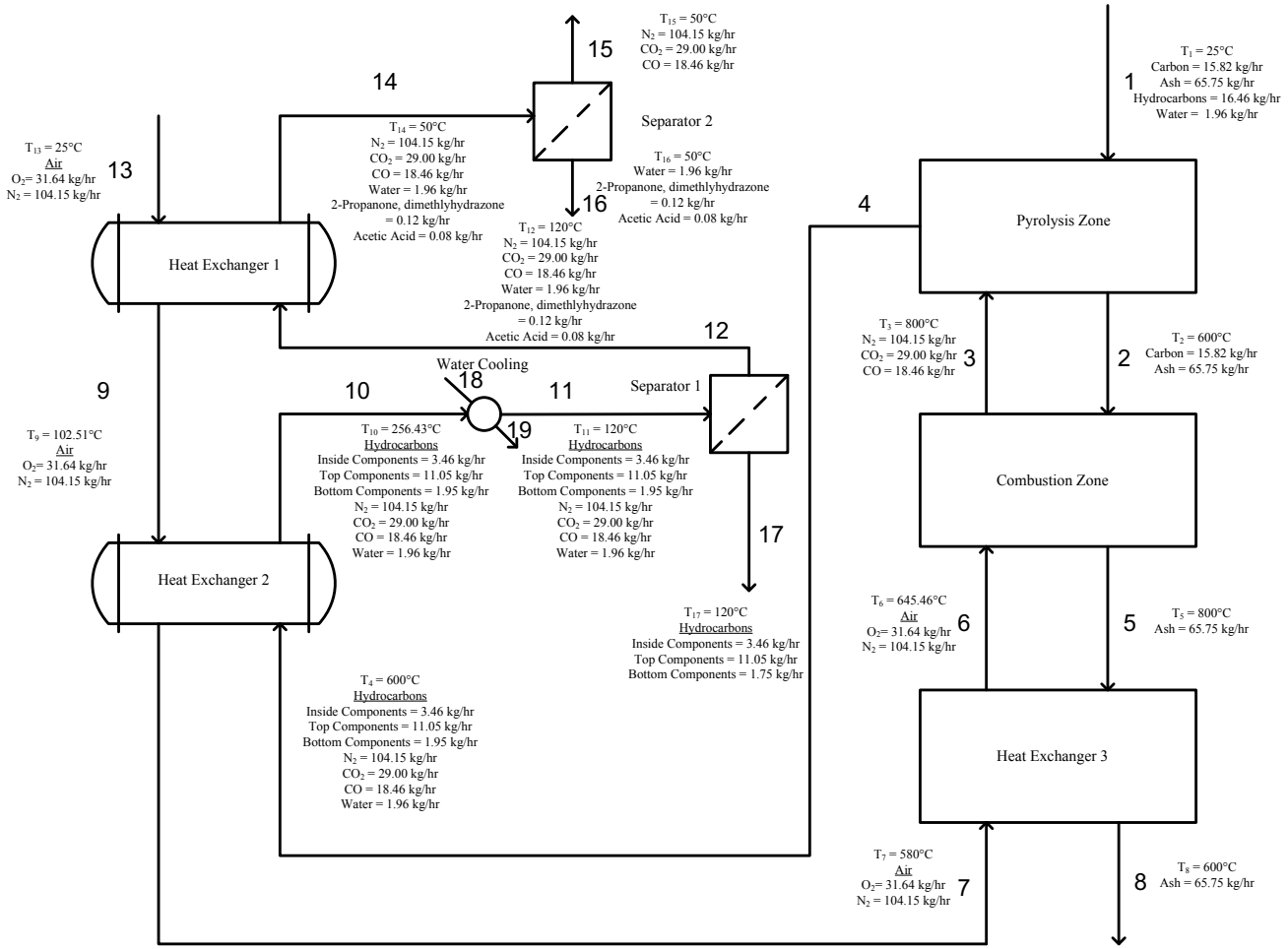


Figure 5.5: Mass and Energy Balance Circuit for High Ash Coal Sample (65.75%)

Table 5.3: Showing the Stream Properties for 65.75% Ash Content Coal

	Stream																
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
Temperature (ºC)	25	600	800	600	800	634.9	580	600	100.44	252.72	120	120	25	50	50	50	120
Components (kg/hr)																	
Carbon	15.82	15.82															
Ash	65.75	65.75			65.75			65.75									
Volatiles	16.46																
Inside Components				3.46						3.46	3.46						3.46
Top Components				11.05						11.05	11.05						11.05
Bottom Components				1.95						1.95	1.95						1.75
Water	1.96			1.96						1.96	1.96	1.96		1.96		1.9	
N2			104.15	104.15		104.15	104.15		104.15	104.15	104.15	104.15	104.15	104.15	104.15		
CO2			29.00	29.00						29.00	29.00	29.00		29.00	29.00		
CO			18.46	18.46						18.46	18.46	18.46		18.46	18.46		
O2						31.64	31.64		31.64				31.64				
2-Propanone,dimethylhydrazone												0.12		0.12		0.12	
Acetic Acid												0.08		0.08		0.08	

Figure 5.3, which shows the results obtained for a low ash sample (35.6%) also indicates that there is excess energy available within the system. In heat exchanger 3, the air is heated via exchange with hot ash. However, the ash is cooled to within 20°C of the air temperature entering, it could be cooled to lower temperature if more heat is required. The hydrocarbons which exit heat exchanger 2 need to be further cooled using cooling water, which creates steam which could be utilised as a heating source. The excess heat could be utilised to make up for heat losses as these were not considered in the above calculations.

Figures 5.4 - 5.5, which are high ash samples also display the same trends observed for the low ash samples. There is sufficient energy available to operate the process and there is extra available from the hydrocarbon and ash cooling.

An examination of the energy balance revealed that the condensation of the liquid hydrocarbon product could not rely only on cooling by the incoming air alone. Additional cooling is required and the most convenient way of achieving this is to use a utility heat exchanger. A temperature of 110^0C was chosen for superheated steam production, to ensure that the product contained no liquid. Table 5.4 shows the amount of steam produced (assuming no heat losses), for the various samples.

Table 5.4: Steam available at 110°C

% Ash Content	Steam Available (kg/hr)
25.69	24.12
32.93	23.92
33.75	18.93
35.64	19.1
63.23	14.04
65.75	13.03

The amount of steam available reduces as the ash content increases. This is due to reduction in the amount of carbon available for combustion and a change in the ratio of hydrocarbon to fixed carbon.

5.3.4 Excess Energy Available from Combustion

The calculations for the combustion zone were based on an assumed combustion temperature and hence the temperature of the streams leaving this (perfectly mixed) zone were defined. The energy released by combustion was used to calculate the 'excess energy available', which is illustrated in Figure 5.6 for combustion at 800^0C. As the ash content increases, less excess energy is available, as there is less carbon to burn and more ash to heat up to combustion temperature. The actual figures shown by Figure 5.6 are not significant but it is indicative that there is excess energy available.

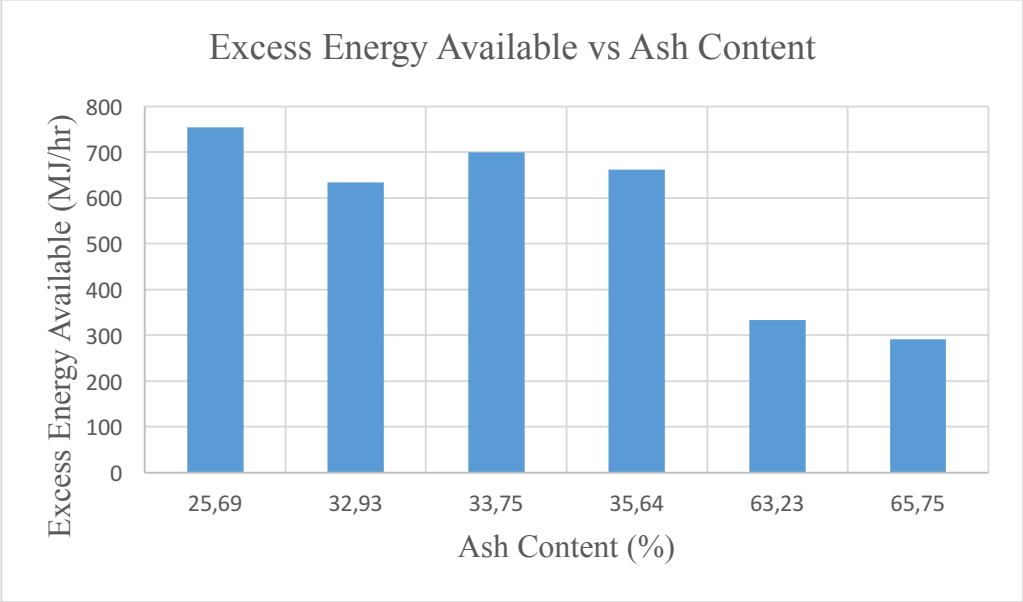


Figure 5.6: Showing the excess Energy Available from the Combustion Zone operating at 800^0C

5.4 Mass and Energy Balance for Pyrolysis at 700^0C

While the data suggests that a temperature of 600°C may be adequate for pyrolysis, a higher temperature would ensure faster and more complete pyrolysis. The final set of pyrolysis experiments were conducted at 700°C and hence the mass and energy balance below is designed to test pyrolysis at 700°C. A higher combustion temperature is required and 950°C was selected, which should also result in more efficient combustion, but it requires more pre-heating of the air. The data from the sample with the highest ash content (65.75%) was used, as a high ash content is a real test of the concept. It is important to note that there is still some excess energy available under these conditions. There is also a positive availability from subsequent gas cooling of steam available at 110°C. Figure 5.7 shows the calculated data.

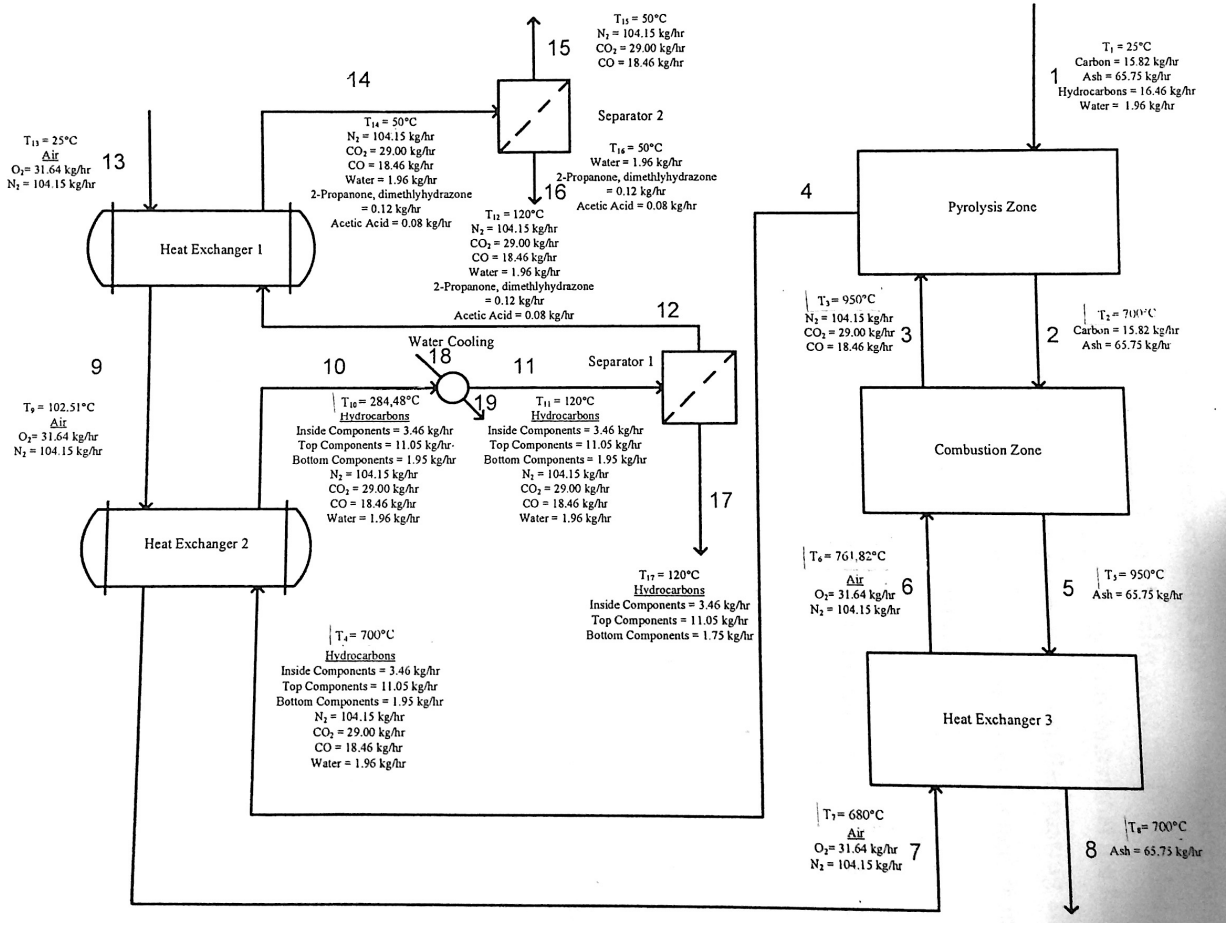


Figure 5.7: Mass and Energy Balance Circuit for High Ash Coal Sample (65.75%)

Chapter 6

Conclusions and Recommendations

6.1 Conclusions

- The initial pyrolysis and combustion experiments showed incomplete combustion of particles with a mass of about 40g. (These particles were partly rounded and had dimensions of about 25mm x 30mm x 25mm). It was concluded that the feed to the proposed counter-current rector should be crushed to a smaller passing size. The subsequent tests were conducted using particles whose mass ranged from 7g to 23g. These tests demonstrated complete combustion.

- The effect of feed size was not tested further, as the main focus was the effect of temperature and residence time on pyrolysis.

- Coal with a high mineral content (above 50% ash) is more suited for the extraction of volatiles (and combustion of char), as it retains its original structure and does not disintegrate into powder. This makes a counter-current flow of gas and solids possible.

- A significant portion of the liquid pyrolysis product remained inside the reactor and exit tube. The rate of collection of the liquid outside the reactor was only an indication of recovery, and modelling was not possible.

- GCMS analysis showed that a large proportion of the product consisted of phenols. This is seen as an attractive feature, as this type of compound can be used in many industrial applications.

- The overall water content was low (less than 2 per cent).

- The mass and energy balances, (which did not consider heat loss), showed that a high mineral content in the feed could be accommodated. The energy balance

across the pyrolysis zone had excess energy available, even when the temperature was raised to 700^0C.

- The simulation of cooling of the volatile products required the use of heat exchange with water. The rate of production of low pressure steam was calculated and it was concluded that this steam could be used to reduce external heat loss from the combustion and pyrolysis zones.

- The results suggest that that the proposed counter-current process can work on coal with a high mineral content.

6.2 Recommendations

- Samples coal seams which are currently discarded from the Waterberg coalfields should be obtained for further tests.

- The reactor for laboratory experiments should be re-designed, to enable accurate measurement of the rate of pyrolysis (e.g. by using a thermo-balance).

- Partial condensation of the products of pyrolysis should be avoided, to make it possible to measure and model the pyrolysis process.

- It is suggested that the liquid product be distilled, to separate it into a few fractions, prior to separate analysis using the Karl Fischer method and a GCMS.

- Additional calculations should be done on the heat and energy balance for the proposed reactor, particularly the heat loss from the hot zones of the reactor, given a realistic size of the reactor and the conductivity of typical lagging. These calculations could also take into account the availability of low-grade steam.

- The value of the products and the availability of discarded coal from existing mining and coal washing operations should be assessed. This analysis may have to include the cost of transporting the products to markets in Sothern Africa.

- If the above analysis produces interesting results, this could then lead to pilot-plant experiments and a re-assessment of mining other parts of the Waterberg coal field.

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Appendix A

Additional Data

A-1 Experimental Procedure – Additional Information

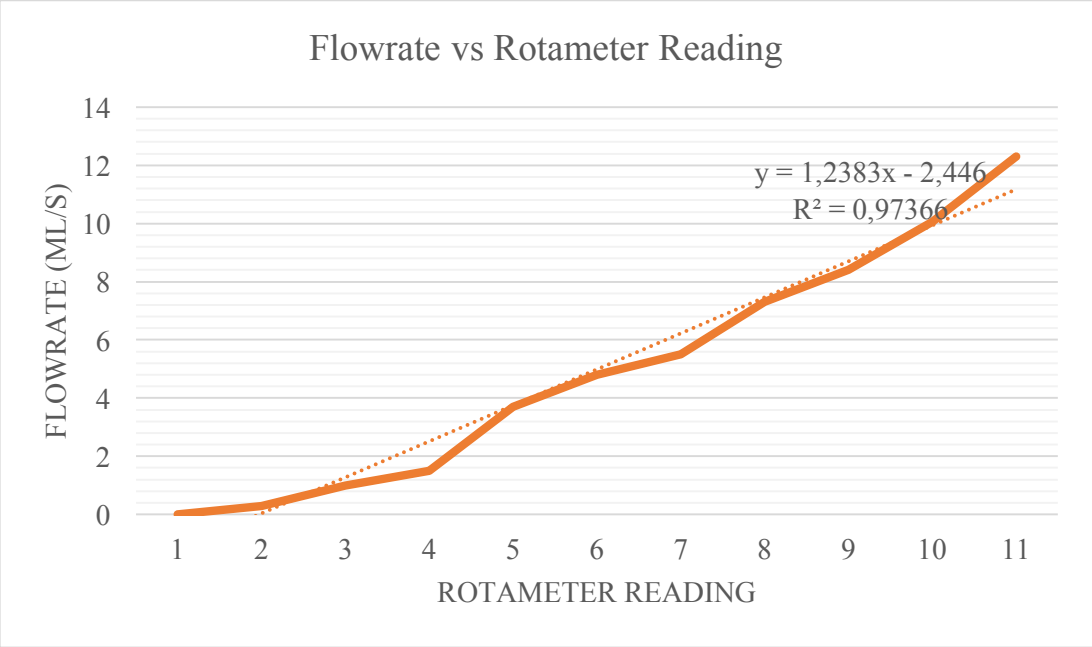


Figure A-1: Rotameter Calibration Curve

GCMS Method

The GCMS has Realtime and Postrun icons. The Realtime icon is where the method conditions are either setup or downloaded for the analysis. On conclusion of the run the data can be verified on Postrun where the integration is coupled with the data library to provide the list of compounds.

GCMS Start-up and Shutdown

Start-Up

Click on the GCMS Real time Icon

- Login with password to start up Lab Solution Software.
- Data acquisition software opens automatically.

- Open vacuum control windows by clicking on the Vacuum Control icon.
- Click on Advanced to open all GCMS setup icons.
- Click on auto start function to stat vacuum system.
- All grey GCMS icon buttons should turn green. Wait for at least four hours to get a good vacuum or until the small arrow in the Vacuum icon shifts to green.
- After the vacuum is achieved, click on the Auto Tuning icon in the assistant bar.
- Check the Auto tuning results, if all the results are okay the instrument is ready for analysis.
- Inject Sample and allow for analysis to occur.

Shutdown

- Click on the Vacuum Control icon and choose the vacuum control windows.
- Click on Advance, then Auto Shutdown.

Liquid Sample Titration (from Good Titration Practice™ in Karl Fischer Titration, Pg 44)

- The syringe was rinsed, by filling with sample and shaking it. The sample was then discarded into a waste container. Repeat twice or thrice.
- The syringe was then filled with sample and weighed in a balance, the mass was recorded.
- Start titration method by pressing 'Start' button.
- Inject the sample through the septum into the titration cell.
- Weigh the syringe again and note the weight. The difference is the amount of sample injected into the cell.
- Enter the sample size into the titrator.
- Start the Titration.
- Repeat this procedure thrice for accuracy.
- Note down the water content from the Interface.

A-2: Preliminary Pyrolysis and Combustion of 'Large' Coal pieces at temperatures between 300°C - 700°C

Table A.1: Raw Data collected during Preliminary Pyrolysis tests for 'Large Coal' pieces over a temperature range of 300°C - 700°C

Ash Content (%)	**38.55**	**55.52**	**70.11**	**75.45**
Initial Mass of Coal Sample (g)	40.6	33.1	40.1	48.7
Final Mass of Coal Sample (g)	31.6	26.6	34.1	41.9
Mass of Reactor +Thermocouple before Pyrolysis (g)	1193.1	1195.2	1194.5	1196
Mass of Reactor + Thermocouple after Pyrolysis (g)	1200.6	1199.5	1199.8	1199.9

Table A.2: Vial Masses for Volatile Samples Collected during Preliminary Pyrolysis tests for 'Large' Coal pieces over a temperature range of 300°C - 700°C

Ash Content (%)	38.55		55.52		70.11		75.45	
Temperature (°C)	Initial Vial Mass (g)	Final Vial Mass (g)	Initial Vial Mass (g)	Final Vial Mass (g)	Initial Vial Mass (g)	Final Vial Mass (g)	Initial Vial Mass (g)	Final Vial Mass (g)
300	11.30	11.60	11.35	11.86	10.45	10.58	11.34	11.45
400	11.30	12.10	11.22	11.38	11.33	11.35	11.23	11.32
500	12.30	12.31	11.60	12.44	11.34	11.39	11.57	11.81
600	11.27	11.33	10.44	10.72	11.23	11.60	10.45	10.92
700	11.32	11.33	11.37	11.43	11.53	11.56	11.33	12.95

Table A.3: Summary of Raw and Calculated Data obtained during Preliminary Pyrolysis and Combustion Experiments for 'Large' Coal pieces over a temperature range of 300°C - 700°C

Ash Content (%)	**38.55**	**55.52**	**70.11**	**75.45**
Mass of Coal Sample before Pyrolysis (g)	40.60	33.10	40.10	48.70
Mass of Coal Sample after Pyrolysis (g)	31.60	26.60	34.10	41.90
Mass Lost from Coal Sample (g)	9.00	6.50	6.00	6.80
Mass Collected in Vial (g)	1.18	1.84	0.59	2.55
Mass of Reactor + Thermocouple before Pyrolysis (g)	1193.10	1195.20	1194.50	1196.00
Mass of Reactor + Thermocouple after Pyrolysis (g)	1200.60	1199.50	1199.80	1199.90
Mass of Liquid collected in the Reactor (g)	7.50	4.30	5.30	3.90
% Recovery of Volatiles	96.40	94.52	98.23	94.92
% Volatiles (Water + Hydrocarbons)	22.17	19.64	14.96	13.96
Ash Remaining (g)	15.65	18.38	28.11	36.74
% Ash	38.55	55.52	70.11	75.45
% Carbon	39.28	24.85	14.93	10.59
Mass Recovered (g)	8.68	6.14	5.89	6.45
Non-Ash Mass (g)	7.00	4.60	2.70	2.10

Table A.4: Summary of Raw and Calculated Data obtained during Preliminary Combustion Experiments for 'Large' Coal pieces over a temperature range of 300°C - 700°C

Ash Content (%)	Temperature (°C)	Time (mins)	Mass Sample (g) + Mass of Crucible	% Mass Lost
38.55	26.9°C - 300°C	0	33.5	0.00
		75	32.8	4.67
	300°C	75	32.8	4.67
		97.5	32.8	4.67
	300°C - 400°C	97.5	32.8	4.67
		142.5	32.6	6.00
	400°C	142.5	32.6	6.00
		165	32.6	6.00
	400°C - 500°C	165	32.6	6.00
		210	32.3	8.00
	500°C	210	32.3	8.00
		232.5	31.4	14.00
	500°C - 600°C	232.5	31.4	14.00
		277.5	29.8	24.67
	600°C	277.5	29.8	24.67
		300	28.9	30.67
	600°C - 700°C	300	28.9	30.67
		345	27.3	41.33
	700°C	345	27.3	41.33
		367.5	26.5	46.67
55.52	26.9°C - 300°C	0	31.8	0.00
		75	31.5	2.26
	300°C	75	31.5	2.26
		97.5	31.5	2.26
	300°C - 400°C	97.5	31.5	2.26
		142.5	31.5	2.26
	400°C	142.5	31.5	2.26
		165	31.4	3.01
	400°C - 500°C	165	31.4	3.01

		210	30.6	9.02
	500°C	210	30.6	9.02
		232.5	30.4	10.53
	500°C - 600°C	232.5	30.4	10.53
		277.5	29.5	17.29
	600°C	277.5	29.5	17.29
		300	28.9	21.80
	600°C - 700°C	300	28.9	21.80
		345	27.9	29.32
	700°C	345	27.9	29.32
		367.5	27.2	34.59
70.11	26.9°C - 300°C	0	37	0.00
		75	36.9	0.62
	300°C	75	36.9	0.62
		97.5	36.8	1.23
	300°C - 400°C	97.5	36.8	1.23
		142.5	36.7	1.85
	400°C	142.5	36.7	1.85
		165	36.7	1.85
	400°C - 500°C	165	36.7	1.85
		210	36.7	1.85
	500°C	210	36.7	1.85
		232.5	36.5	3.09
	500°C - 600°C	232.5	36.5	3.09
		277.5	35.5	9.26
	600°C	277.5	35.5	9.26
		300	35.1	11.73
	600°C - 700°C	300	35.1	11.73
		345	34.5	15.43
	700°C	345	34.5	15.43
		367.5	34.3	16.67
75.45	26.9°C - 300°C	0	41.2	0.00
		75	41.2	0.00
	300°C	75	41.2	0.00
		97.5	41.1	0.48

	300°C - 400°C	97.5	41.1	0.48
		142.5	41.1	0.48
	400°C	142.5	41.1	0.48
		165	41.1	0.48
	400°C - 500°C	165	41.1	0.48
		210	40.9	1.45
	500°C	210	40.9	1.45
		232.5	40.8	1.93
	500°C - 600°C	232.5	40.8	1.93
		277.5	40.5	3.38
	600°C	277.5	40.5	3.38
		300	40.1	5.31
	600°C - 700°C	300	40.1	5.31
		345	39.3	9.18
	700°C	345	39.3	9.18
		367.5	39.1	10.14

A-3: Pyrolysis and Combustion of Repeat Tests (New Particle Size) at temperatures between 300°C - 700°C

Table A.5: Raw Data collected during Pyrolysis for Repeat Tests (New Particle Size) over a temperature range of 300°C - 700°C

Ash Content (%)	18.62	32.41	33.30	34.6	67.55	69.43	70.77	79.1
Initial Mass of Coal Sample (g)	6.98	9.56	17.72	8.38	15.40	13.68	12.29	23.51
Final Mass of Coal Sample (g)	4.60	7.00	13.10	6.30	12.70	11.10	10.70	20.80
Mass of Reactor +Thermocouple before Pyrolysis (g)	1199.50	1199.00	1199.40	1198.80	1198.00	1199.70	1197.60	1197.50
Mass of Reactor + Thermocouple after Pyrolysis (g)	1201.70	1201.30	1203.10	1200.70	1200.40	1201.80	1199.10	1199.60

Table A.6: Vial Masses for Volatile Samples Collected during Pyrolysis for Repeat Tests (New Particle Size) over a temperature range of 300°C - 700°C

Ash Content (%)	18.62		32.41		33.30		34.60	
Temperature (°C)	Initial Vial Mass (g)	Final Vial Mass (g)	Initial Vial Mass (g)	Final Vial Mass (g)	Initial Vial Mass (g)	Final Vial Mass (g)	Initial Vial Mass (g)	Final Vial Mass (g)
300	9.2790	9.2805	9.3971	9.4166	10.4696	10.5471	12.0334	12.0652
400	9.2645	9.3003	9.2691	9.3567	11.5447	11.9866	11.3999	11.4386
500	9.3053	9.3556	9.2784	9.4130	11.2221	11.4193	11.3316	11.3574
600	9.4492	9.4518	9.3513	9.3519	11.5902	11.5929	11.3487	11.3500
700	9.2465	9.2479	10.1553	10.1569	11.3931	11.3932	11.3937	11.3956

Table A.7: Vial Masses for Volatile Samples Collected during Pyrolysis for Repeat Tests (New Particle Size) over a temperature range of 300°C - 700°C Continued ..

Ash Content (%)	67.55		69.43		70.77		79.10	
Temperature (°C)	Initial Vial Mass (g)	Final Vial Mass (g)	Initial Vial Mass (g)	Final Vial Mass (g)	Initial Vial Mass (g)	Final Vial Mass (g)	Initial Vial Mass (g)	Final Vial Mass (g)
300	11.4596	11.4596	12.0329	12.0329	11.6595	11.6595	11.3640	11.3646
400	11.3180	11.3180	12.2517	12.2645	12.2172	12.2206	12.2368	12.2602
500	11.3316	11.3544	11.3129	11.3170	11.3649	11.3658	11.7817	11.7852

600	11.2560	11.4455	12.4588	12.8283	11.3118	11.3118	11.4321	11.9624
700	11.2788	11.2789	11.3034	11.3034	11.2475	11.2475	11.2421	11.2421

Table A.8: Summary of Raw and Calculated Data obtained during Pyrolysis and Combustion Experiments for Repeat Tests (New Particle Size) over a temperature range of 300°C - 700°C

Ash Content (%)	18.62	32.41	33.30	34.60	67.55	69.43	70.77	79.10
Mass of Coal Sample before Pyrolysis (g)	6.98	9.56	17.72	8.38	15.40	13.68	12.29	23.51
Mass of Coal Sample after Pyrolysis (g)	4.60	7.00	13.10	6.30	12.70	11.10	10.70	20.80
Mass Lost from Coal Sample (g)	2.38	2.56	4.62	2.08	2.70	2.58	1.59	2.71
Mass Collected in Vial (g)	0.09	0.24	0.72	0.10	0.21	0.39	0.00	0.56
Mass of Reactor + Thermocouple before Pyrolysis (g)	1199.50	1199.00	1199.40	1198.80	1198.00	1199.70	1197.60	1197.50
Mass of Reactor + Thermocouple after Pyrolysis (g)	1201.70	1201.30	1203.10	1200.70	1200.40	1201.80	1199.10	1199.60
Mass of Liquid collected in the Reactor (g)	2.20	2.30	3.70	1.90	2.40	2.10	1.50	2.10
% Recovery of Volatiles	96.19	99.19	95.74	96.12	96.92	96.26	94.37	97.91
Percent Volatiles (Water + Hydrocarbons)	34.12	26.81	26.06	24.82	17.51	18.88	12.97	11.54
Ash Remaining (g)	1.30	3.10	5.90	2.90	10.40	9.50	8.70	18.60
%Ash	18.62	32.41	33.30	34.60	67.55	69.43	70.77	79.10
%Carbon	47.26	40.78	40.64	40.57	14.94	11.69	16.27	9.36
Mass Recovered (g)	2.29	2.54	4.42	2.00	2.61	2.49	1.50	2.66
Non-Ash Mass (g)	3.30	3.90	7.20	3.40	2.30	1.60	2.00	2.20

Table A.9: Summary of Raw and Calculated Data obtained during Combustion Experiments for Repeat Tests (New Particle Size) over a temperature range of 300°C - 700°C

Ash Content (%)	Temperature (°C)	Time (mins)	Mass Sample (g) + Mass of Crucible	% Mass Lost
18.62	26.9°C - 300°C	0	23.6	0.00
		75	23.4	4.35
	300°C	75	23.4	4.35
		97.5	23.4	4.35
	300°C - 400°C	97.5	23.4	4.35
		142.5	23.4	4.35
	400°C	142.5	23.4	4.35
		165	23.4	4.35
	400°C - 500°C	165	23.4	4.35
		210	22.1	32.61
	500°C	210	22.1	32.61
		232.5	21.6	43.48
	500°C - 600°C	232.5	21.6	43.48
		277.5	20.8	60.87
	600°C	277.5	20.8	60.87
		300	20.6	65.22
	600°C - 700°C	300	20.6	65.22
		345	20.3	71.74
	700°C	345	20.3	71.74
		367.5	20.3	71.74
32.41	26.9°C - 300°C	0	26.3	0.00
		75	26	4.29
	300°C	75	26	4.29
		97.5	26	4.29
	300°C - 400°C	97.5	26	4.29
		142.5	26	4.29
	400°C	142.5	26	4.29
		165	26	4.29

	400°C - 500°C	165	26	4.29
		210	24.9	20.00
	500°C	210	24.9	20.00
		232.5	24.3	28.57
	500°C - 600°C	232.5	24.3	28.57
		277.5	23.4	41.43
	600°C	277.5	23.4	41.43
		300	23.2	44.29
	600°C - 700°C	300	23.2	44.29
		345	22.6	52.86
	700°C	345	22.6	52.86
		367.5	22.4	55.71
33.30	26.9°C - 300°C	0	34.7	0.00
		75	34.1	4.58
	300°C	75	34.1	4.58
		97.5	34.1	4.58
	300°C - 400°C	97.5	34.1	4.58
		142.5	34	5.34
	400°C	142.5	34	5.34
		165	33.9	6.11
	400°C - 500°C	165	33.9	6.11
		210	33	12.98
	500°C	210	33	12.98
		232.5	31.7	22.90
	500°C - 600°C	232.5	31.7	22.90
		277.5	29.9	36.64
	600°C	277.5	29.9	36.64
		300	29.1	42.75
	600°C - 700°C	300	29.1	42.75
		345	28	51.15
	700°C	345	28	51.15
		367.5	27.5	54.96
34.60	26.9°C - 300°C	0	27.1	0.00
		75	27.1	0.00
	300°C	75	27.1	0.00

		97.5	27.1	0.00
	300°C - 400°C	97.5	27.1	0.00
		142.5	27.1	0.00
	400°C	142.5	27.1	0.00
		165	27.1	0.00
	400°C - 500°C	165	27.1	0.00
		210	26	17.46
	500°C	210	26	17.46
		232.5	25.7	22.22
	500°C - 600°C	232.5	25.7	22.22
		277.5	24.7	38.10
	600°C	277.5	24.7	38.10
		300	24.4	42.86
	600°C - 700°C	300	24.4	42.86
		345	23.7	53.97
	700°C	345	23.7	53.97
		367.5	23.7	53.97
67.55	26.9°C - 300°C	0	31.7	0.00
		75	31.5	1.57
	300°C	75	31.5	1.57
		97.5	31.5	1.57
	300°C - 400°C	97.5	31.5	1.57
		142.5	31.5	1.57
	400°C	142.5	31.5	1.57
		165	31.5	1.57
	400°C - 500°C	165	31.5	1.57
		210	31.2	3.94
	500°C	210	31.2	3.94
		232.5	31.2	3.94
	500°C - 600°C	232.5	31.2	3.94
		277.5	30.5	9.45
	600°C	277.5	30.5	9.45
		300	30.2	11.81
	600°C - 700°C	300	30.2	11.81

		345	29.5	17.32
	700°C	345	29.5	17.32
		367.5	29.4	18.11
69.43	26.9°C - 300°C	0	30.4	0.00
		75	30.2	1.80
	300°C	75	30.2	1.80
		97.5	30.2	1.80
	300°C - 400°C	97.5	30.2	1.80
		142.5	30.2	1.80
	400°C	142.5	30.2	1.80
		165	30.2	1.80
	400°C - 500°C	165	30.2	1.80
		210	30.2	1.80
	500°C	210	30.2	1.80
		232.5	30	3.60
	500°C - 600°C	232.5	30	3.60
		277.5	29.4	9.01
	600°C	277.5	29.4	9.01
		300	29.2	10.81
	600°C - 700°C	300	29.2	10.81
		345	28.9	13.51
	700°C	345	28.9	13.51
		367.5	28.8	14.41
70.77	26.9°C - 300°C	0	29.5	0.00
		75	29.4	0.93
	300°C	75	29.4	0.93
		97.5	29.3	1.87
	300°C - 400°C	97.5	29.3	1.87
		142.5	29.3	1.87
	400°C	142.5	29.3	1.87
		165	29.3	1.87
	400°C - 500°C	165	29.3	1.87
		210	29.3	1.87
	500°C	210	29.3	1.87
		232.5	29.1	3.74

	500°C - 600°C	232.5	29.1	3.74
		277.5	28.4	10.28
	600°C	277.5	28.4	10.28
		300	28.1	13.08
	600°C - 700°C	300	28.1	13.08
		345	27.7	16.82
	700°C	345	27.7	16.82
		367.5	27.5	18.69
79.10	26.9°C - 300°C	0	41.9	0.00
		75	41.7	0.96
	300°C	75	41.7	0.96
		97.5	41.7	0.96
	300°C - 400°C	97.5	41.7	0.96
		142.5	41.7	0.96
	400°C	142.5	41.7	0.96
		165	41.7	0.96
	400°C - 500°C	165	41.7	0.96
		210	41.6	1.44
	500°C	210	41.6	1.44
		232.5	41.3	2.88
	500°C - 600°C	232.5	41.3	2.88
		277.5	40.5	6.73
	600°C	277.5	40.5	6.73
		300	40.3	7.69
	600°C - 700°C	300	40.3	7.69
		345	39.9	9.62
	700°C	345	39.9	9.62
		367.5	39.7	10.58

A-4: Pyrolysis and Combustion of Tests at a temperature of 700°C for 1 hour

Table A.10: Raw Data collected during Pyrolysis for tests at a temperature of 700°C for 1 hour

Ash Content (%)	31.70	32.03	33.89	35.54	37.31	40.19	42.26	46.71	47.23	73.01	82.18	82.30
Initial Mass of Coal Sample (g)	8.48	11.88	11.21	11.90	13.62	9.40	15.90	13.78	12.16	16.57	18.37	13.97
Final Mass of Coal Sample (g)	5.89	8.80	8.42	9.13	10.08	7.08	11.92	10.74	9.24	14.62	16.10	12.20
Mass of Reactor +Thermocouple before Pyrolysis (g)	1197.20	1197.10	1197.00	1197.10	1197.20	1197.00	1197.10	1197.30	1197.00	1197.80	1197.40	1197.00
Mass of Reactor + Thermocouple after Pyrolysis (g)	1199.20	1198.50	1199.40	1199.20	1199.90	1198.30	1199.20	1198.90	1199.30	1199.00	1198.40	1198.40

Table A.11: Vial Masses for Volatile Samples Collected during Pyrolysis for tests at a temperature of 700°C every 15 minutes

Ash Content (%)	31.70		32.03		33.89		35.54	
Time (minutes)	Initial Vial Mass (g)	Final Vial Mass (g)	Initial Vial Mass (g)	Final Vial Mass (g)	Initial Vial Mass (g)	Final Vial Mass (g)	Initial Vial Mass (g)	Final Vial Mass (g)
15	11.2468	11.4699	12.1643	13.4800	11.3109	11.5681	11.4695	12.0238
30	11.3852	11.5798	11.2857	11.4471	11.2796	11.3473	11.5272	11.5292
45	11.4276	11.5232	11.1927	11.2086	11.3517	11.3540	11.1984	11.1985
60	11.2676	11.2949	11.3788	11.3793	9.3845	9.3845	11.3115	11.3116

Table A.12: Vial Masses for Volatile Samples Collected during Pyrolysis tests at a temperature of 700°C every 15 minutes

Ash Content (%)	37.31		40.19		42.26		46.71	
Time (minutes)	Initial Vial Mass (g)	Final Vial Mass (g)	Initial Vial Mass (g)	Final Vial Mass (g)	Initial Vial Mass (g)	Final Vial Mass (g)	Initial Vial Mass (g)	Final Vial Mass (g)
15	11.3211	11.9633	11.3976	12.4018	11.3934	12.9491	11.2956	12.5731
30	11.2202	11.2493	11.3100	11.3107	12.2042	12.4358	11.2503	11.3019
45	11.5126	11.5199	11.1616	11.1664	11.3619	11.3620	11.7211	11.7219
60	11.3843	11.3847	11.4216	11.4219	11.3597	11.3600	11.7876	11.7886

Table A.13: Vial Masses for Volatile Samples Collected during Pyrolysis for tests at a temperature of 700°C every 15 minutes

Ash Content (%)	47.23		73.01		82.18		82.30	
Time (minutes)	Initial Vial Mass (g)	Final Vial Mass (g)	Initial Vial Mass (g)	Final Vial Mass (g)	Initial Vial Mass (g)	Final Vial Mass (g)	Initial Vial Mass (g)	Final Vial Mass (g)
15	12.2145	12.6234	11.1336	11.7789	10.4696	11.6723	12.0097	12.3454
30	11.3433	11.3436	11.4290	11.4291	11.5921	11.6314	10.4567	10.4591
45	11.2150	11.2166	12.0321	12.0344	11.4814	11.4814	12.4896	12.4896
60	11.6589	11.6624	11.5737	11.5743	12.0298	12.0298	11.3221	11.3221

Table A.14: Summary of Raw and Calculated Data obtained during Pyrolysis and Combustion Experiments for tests at a temperature of 700°C for 1 hour

Ash Content (%)	31.70	32.03	33.89	35.54	37.31	40.19
Mass of Coal Sample before Pyrolysis (g)	8.48	11.88	11.21	11.90	13.62	9.40
Mass of Coal Sample after Pyrolysis (g)	5.89	8.80	8.42	9.13	10.08	7.08
Mass Lost from Coal Sample (g)	2.59	3.07	2.80	2.77	3.54	2.32
Mass Collected in Vial (g)	0.54	1.49	0.33	0.56	0.68	1.01
Mass of Reactor + Thermocouple before Pyrolysis (g)	1197.20	1197.10	1197.00	1197.10	1197.20	1197.00
Mass of Reactor + Thermocouple after Pyrolysis (g)	1199.20	1198.50	1199.40	1199.20	1199.90	1198.30
Mass of Liquid collected in the Reactor (g)	2.00	1.40	2.40	2.10	2.70	1.30
% Recovery of Volatiles	98.06	94.17	97.51	95.90	95.42	99.46
% Volatiles (Water + Hydrocarbons)	30.56	25.87	24.94	23.28	25.99	24.71
Ash Remaining (g)	2.69	3.80	3.80	4.23	5.08	3.78
% Ash	31.70	32.03	33.89	35.54	37.31	40.19
% Carbon	37.74	42.10	41.17	41.18	36.70	35.11
Mass Recovered (g)	2.54	2.89	2.73	2.66	3.38	2.31
Non-Ash Mass (g)	3.20	5.00	4.60	4.90	5.00	3.30

Table A.15: Summary of Raw and Calculated Data obtained during Pyrolysis Experiments for tests at a temperature of 700°C for 1 hour

Ash Content (%)	**42.26**	**46.71**	**47.23**	**73.01**	**82.18**	**82.30**
Mass of Coal Sample before Pyrolysis (g)	15.90	13.78	12.16	16.57	18.37	13.97
Mass of Coal Sample after Pyrolysis (g)	11.92	10.74	9.24	14.62	16.10	12.20
Mass Lost from Coal Sample (g)	3.98	3.04	2.91	1.95	2.28	1.77
Mass Collected in Vial (g)	1.79	1.33	0.41	0.65	1.24	0.34
Mass of Reactor + Thermocouple before Pyrolysis (g)	1197.10	1197.30	1197.00	1197.80	1197.40	1197.00
Mass of Reactor + Thermocouple after Pyrolysis (g)	1199.20	1198.90	1199.30	1199.00	1198.40	1198.40
Mass of Liquid collected in the Reactor (g)	2.10	1.60	2.30	1.20	1.00	1.40
% Recovery of Volatiles	97.66	96.37	93.14	94.70	98.50	98.01
% Volatiles (Water + Hydrocarbons)	25.03	22.07	23.97	11.78	12.39	12.69
Ash Remaining (g)	6.72	6.44	5.74	12.10	15.10	11.50
% Ash	42.26	46.71	47.23	73.01	82.18	82.30
% Carbon	32.70	31.21	28.79	15.22	5.44	5.01
Mass Recovered (g)	3.89	2.93	2.71	1.85	2.24	1.74
Non-Ash Mass (g)	5.20	4.30	3.50	2.50	1.00	0.70

Table A.16: Summary of Raw and Calculated Data obtained during Combustion Experiments for tests at a temperature of 700°C for 1 hour

Ash Content (%)	Temperature (°C)	Time (mins)	Mass Sample (g) + Mass of Crucible	% Mass Lost
31.7	26.9°C - 300°C	0	24.1	0.00
		75	24.1	0.00
	300°C	75	24.1	0.00
		97.5	24.1	0.00
	300°C - 400°C	97.5	24.1	0.00
		142.5	24.1	0.00
	400°C	142.5	24.1	0.00
		165	24.1	0.00
	400°C - 500°C	165	24.1	0.00
		210	23.3	13.59
	500°C	210	23.3	13.59
		232.5	22.6	25.48
	500°C - 600°C	232.5	22.6	25.48
		277.5	21.3	47.55
	600°C	277.5	21.3	47.55
		300	21	52.65
	600°C - 700°C	300	21	52.65
		345	20.9	54.35
	700°C	345	20.9	54.35
		367.5	20.9	54.35
32.03	26.9°C - 300°C	0	27.4	0.00
		75	27.3	1.14
	300°C	75	27.3	1.14
		97.5	27.3	1.14
	300°C - 400°C	97.5	27.3	1.14
		142.5	27.3	1.14
	400°C	142.5	27.3	1.14
		165	27.3	1.14
	400°C - 500°C	165	27.3	1.14
		210	25.9	17.04
	500°C	210	25.9	17.04
		232.5	24.5	32.94
	500°C - 600°C	232.5	24.5	32.94
		277.5	22.8	52.25
	600°C	277.5	22.8	52.25
		300	22.4	56.79
	600°C - 700°C	300	22.4	56.79

		345	22.4	56.79
	700°C	345	22.4	56.79
		367.5	22.4	56.79
	26.9°C - 300°C	0	27.3	0.00
		75	26.8	5.95
	300°C	75	26.8	5.95
		97.5	26.8	5.95
	300°C - 400°C	97.5	26.8	5.95
		142.5	26.8	5.95
	400°C	142.5	26.8	5.95
		165	26.8	5.95
	400°C - 500°C	165	26.8	5.95
33.89		210	25.2	25.00
	500°C	210	25.2	25.00
		232.5	24.5	33.33
	500°C - 600°C	232.5	24.5	33.33
		277.5	23.7	42.86
	600°C	277.5	23.7	42.86
		300	23.4	46.43
	600°C - 700°C	300	23.4	46.43
		345	22.8	53.57
	700°C	345	22.8	53.57
		367.5	22.7	54.76
	26.9°C - 300°C	0	30	0.00
		75	29.9	1.10
	300°C	75	29.9	1.10
		97.5	29.9	1.10
	300°C - 400°C	97.5	29.9	1.10
		142.5	29.8	2.19
	400°C	142.5	29.8	2.19
		165	29.8	2.19
35.54	400°C - 500°C	165	29.8	2.19
		210	28.4	17.53
	500°C	210	28.4	17.53
		232.5	27.3	29.58
	500°C - 600°C	232.5	27.3	29.58
		277.5	25.9	44.91
	600°C	277.5	25.9	44.91
		300	25.6	48.20
	600°C - 700°C	300	25.6	48.20
		345	25.2	52.58

	700°C	345	25.2	52.58
		367.5	25.1	53.67
37.31	26.9°C - 300°C	0	28.6	0.00
		75	28.6	0.00
	300°C	75	28.6	0.00
		97.5	28.6	0.00
	300°C - 400°C	97.5	28.6	0.00
		142.5	28.6	0.00
	400°C	142.5	28.6	0.00
		165	28.6	0.00
	400°C - 500°C	165	28.6	0.00
		210	27.2	13.88
	500°C	210	27.2	13.88
		232.5	26.1	24.79
	500°C - 600°C	232.5	26.1	24.79
		277.5	24.3	42.65
	600°C	277.5	24.3	42.65
		300	23.7	48.60
	600°C - 700°C	300	23.7	48.60
		345	23.6	49.59
	700°C	345	23.6	49.59
		367.5	23.6	49.59
40.19	26.9°C - 300°C	0	27.7	0.00
		75	27.7	0.00
	300°C	75	27.7	0.00
		97.5	27.7	0.00
	300°C - 400°C	97.5	27.7	0.00
		142.5	27.5	2.83
	400°C	142.5	27.5	2.83
		165	27.5	2.83
	400°C - 500°C	165	27.5	2.83
		210	27.4	4.24
	500°C	210	27.4	4.24
		232.5	26.3	19.78
	500°C - 600°C	232.5	26.3	19.78
		277.5	25.1	36.74
	600°C	277.5	25.1	36.74
		300	24.8	40.97
	600°C - 700°C	300	24.8	40.97
		345	24.5	45.21
	700°C	345	24.5	45.21

		367.5	24.4	46.63
42.26	26.9°C - 300°C	0	32.8	0.00
		75	32.7	0.84
	300°C	75	32.7	0.84
		97.5	32.7	0.84
	300°C - 400°C	97.5	32.7	0.84
		142.5	32.7	0.84
	400°C	142.5	32.7	0.84
		165	32.7	0.84
	400°C - 500°C	165	32.7	0.84
		210	32.3	4.19
	500°C	210	32.3	4.19
		232.5	30.9	15.94
	500°C - 600°C	232.5	30.9	15.94
		277.5	28.7	34.40
	600°C	277.5	28.7	34.40
		300	27.8	41.95
	600°C - 700°C	300	27.8	41.95
		345	27.6	43.62
	700°C	345	27.6	43.62
		367.5	27.6	43.62
46.71	26.9°C - 300°C	0	28.8	0.00
		75	28.7	0.93
	300°C	75	28.7	0.93
		97.5	28.7	0.93
	300°C - 400°C	97.5	28.7	0.93
		142.5	28.7	0.93
	400°C	142.5	28.7	0.93
		165	28.7	0.93
	400°C - 500°C	165	28.7	0.93
		210	27.8	9.31
	500°C	210	27.8	9.31
		232.5	26.6	20.49
	500°C - 600°C	232.5	26.6	20.49
		277.5	25.3	32.60
	600°C	277.5	25.3	32.60
		300	24.7	38.19
	600°C - 700°C	300	24.7	38.19
		345	24.5	40.05
	700°C	345	24.5	40.05
		367.5	24.5	40.05

	26.9°C - 300°C	0	28	0.00
		75	28	0.00
	300°C	75	28	0.00
		97.5	28	0.00
	300°C - 400°C	97.5	28	0.00
		142.5	28	0.00
	400°C	142.5	28	0.00
		165	28	0.00
	400°C - 500°C	165	28	0.00
47.23		210	27	10.82
	500°C	210	27	10.82
		232.5	26.4	17.31
	500°C - 600°C	232.5	26.4	17.31
		277.5	25.1	31.38
	600°C	277.5	25.1	31.38
		300	24.8	34.63
	600°C - 700°C	300	24.8	34.63
		345	24.5	37.87
	700°C	345	24.5	37.87
		367.5	24.5	37.87
	26.9°C - 300°C	0	35.2	0.00
		75	35.2	0.00
	300°C	75	35.2	0.00
		97.5	35.1	0.68
	300°C - 400°C	97.5	35.1	0.68
		142.5	35.1	0.68
	400°C	142.5	35.1	0.68
		165	35.1	0.68
	400°C - 500°C	165	35.1	0.68
73.01		210	35	1.37
	500°C	210	35	1.37
		232.5	35	1.37
	500°C - 600°C	232.5	35	1.37
		277.5	33.9	8.90
	600°C	277.5	33.9	8.90
		300	33.5	11.64
	600°C - 700°C	300	33.5	11.64
		345	32.8	16.44
	700°C	345	32.8	16.44
		367.5	32.7	17.12

82.18	26.9°C - 300°C	0	34.8	0.00
		75	34.6	1.24
	300°C	75	34.6	1.24
		97.5	34.6	1.24
	300°C - 400°C	97.5	34.6	1.24
		142.5	34.6	1.24
	400°C	142.5	34.6	1.24
		165	34.5	1.86
	400°C - 500°C	165	34.5	1.86
		210	34.5	1.86
	500°C	210	34.5	1.86
		232.5	34.4	2.48
	500°C - 600°C	232.5	34.4	2.48
		277.5	34	4.97
	600°C	277.5	34	4.97
		300	33.9	5.59
	600°C - 700°C	300	33.9	5.59
		345	33.9	5.59
	700°C	345	33.9	5.59
		367.5	33.8	6.21
82.3	26.9°C - 300°C	0	32.8	0.00
		75	32.7	0.82
	300°C	75	32.7	0.82
		97.5	32.7	0.82
	300°C - 400°C	97.5	32.7	0.82
		142.5	32.7	0.82
	400°C	142.5	32.7	0.82
		165	32.7	0.82
	400°C - 500°C	165	32.7	0.82
		210	32.5	2.46
	500°C	210	32.5	2.46
		232.5	32.4	3.28
	500°C - 600°C	232.5	32.4	3.28
		277.5	32.1	5.74
	600°C	277.5	32.1	5.74
		300	32.1	5.74
	600°C - 700°C	300	32.1	5.74
		345	32.1	5.74
	700°C	345	32.1	5.74
		367.5	32.1	5.74

A-5: Pyrolysis and Combustion of Tests at a temperature of 700°C for 30 minutes

Table A.17: Raw Data collected during Pyrolysis for tests at a temperature of 700°C for 30 minutes

Ash Content (%)	**25.69**	**32.93**	**33.75**	**35.64**	**63.23**	**65.75**
Mass of Coal Sample before Pyrolysis (g)	8.56	8.81	10.07	10.10	11.86	8.21
Mass of Coal Sample after Pyrolysis (g)	5.72	5.95	7.24	7.24	9.65	6.70
Mass Lost from Coal Sample (g)	2.85	2.86	2.84	2.86	2.21	1.51
Mass of Vial before Pyrolysis (g)	11.24	12.03	11.21	11.68	11.34	11.36
Mass of Vial after Pyrolysis (g)	12.24	13.02	12.28	12.95	12.31	12.48
Mass Collected in Vial (g)	1.00	0.99	1.07	1.27	0.96	1.12
Mass of Reactor + Thermocouple before Pyrolysis (g)	1197.30	1197.10	1197.00	1197.10	1197.30	1197.00
Mass of Reactor + Thermocouple after Pyrolysis (g)	1199.00	1198.80	1198.70	1198.50	1198.50	1197.30
Mass of Liquid collected in the Reactor (g)	1.70	1.70	1.70	1.40	1.20	0.30
% Recovery of Volatiles	94.84	94.07	97.62	93.46	97.94	93.73
% Volatiles (Water + Hydrocarbons)	33.26	32.45	28.18	28.29	18.63	18.43
Ash Remaining (g)	2.20	2.90	3.40	3.60	7.50	5.40
% Ash	25.69	32.93	33.75	35.64	63.23	65.75
% Carbon	41.05	34.62	38.07	36.07	18.14	15.82

Table A.18: Raw and Calculated Data obtained during Karl Fischer Analysis for tests at a temperature of 700°C for 30 minutes

Ash Content (%)	Mass of Sample Injected (g)	Water Concentration (ppm)	Percent Water (%)	Average Percent Water (%)	Fraction of Water
25.69	0.0037	14892	1.49	1.44	0.01
	0.0025	16342	1.63		
	0.0026	11950	1.20		
32.93	0.0878	57914	5.79	5.69	0.06
	0.0122	55345	5.53		
	0.0046	57589	5.76		
33.75	0	0	0.00	0.00	0.00
	0	0	0.00		
	0	0	0.00		
35.64	0.0037	18321	1.83	1.58	0.02
	0.0021	12893	1.29		
	0.0028	16290	1.63		
63.23	0.0025	79644	7.96	8.12	0.08
	0.0045	83978	8.40		
	0.003	80104	8.01		
65.75	0.0025	87653	8.77	8.64	0.09
	0.0034	91233	9.12		
	0.0048	80462	8.05		

Table A.19: Calculated Values for Karl Fischer Analysis for tests at a temperature of 700°C for 30 minutes

Ash Content (%)	25.69	32.93	33.75	35.64	63.23	65.75
Mass Collected in Vial (g)	1.00	0.99	1.07	1.27	0.96	1.12
0.85						
Top Layer Mass (g) -85%	0.85	0.84	0.91	1.08	0.82	0.95
Bottom Layer Mass (g) -15%	0.15	0.15	0.00	0.19	0.14	0.17
Bottom Layer Mass - (Volatiles +Water) - (g)	0.15	0.15	0.00	0.19	0.14	0.17
2ml of Ethanol (g)	1.58	1.58	1.58	1.58	1.58	1.58
Bottom Layer Mass - (Volatiles + Water + Solvent)	1.73	1.73	1.58	1.77	1.72	1.75
Karl Fischer Values	0.01	0.06	0.00	0.02	0.08	0.09
Mass of Water (g)	0.02	0.10	0.00	0.03	0.14	0.15
Mass of Volatiles in the Bottom Layer (g)	0.13	0.05	0.00	0.16	0.00	0.02
Amount of Volatiles (g)	0.98	0.89	0.91	1.24	0.82	0.97
Amount of Water (g)	0.02	0.10	0.00	0.03	0.14	0.15
Total Amount of Volatiles (g)	2.68	2.59	2.61	2.64	2.02	1.27
Total Amount of Water (g)	0.02	0.10	0.00	0.03	0.14	0.15

Table A.20: Calculated Values for Percent Water present in each Sample

Ash Content (%)	Mass of Chemical Compounds in Reactor Tube (g)	Mass of Chemical Compounds collected in Vial (g)	Total Mass of Chemical Compounds (g)	Fraction of Chemical Compounds	Percent of Chemical Compounds in Coal Sample	Mass of Water Collected in Vials (g)	Fraction of Water	Percent of Water present in Coal Sample
25.69	1,7	0,98	2,68	0,31	31,26	0,02	0,00	0,29
32.93	1,7	0,89	2,59	0,29	29,41	0,10	0,01	1,12
33.75	1,7	0,96	2,66	0,26	26,42	0,11	0,01	1,09
35.64	1,4	1,24	2,64	0,26	26,16	0,03	0,00	0,28
63,23	1,2	0,82	2,02	0,17	17,07	0,14	0,01	1,18
65.75	0,3	0,97	1,27	0,15	15,43	0,15	0,02	1,84

Table A.21: Summary of Raw and Calculated Data obtained during Combustion Experiments for tests at a temperature of 700°C for 30 minutes

Ash Content (%)	Temperature (°C)	Time (mins)	Mass Sample (g) + Mass of Crucible	Mass Lost (%)
25.69	26.9°C - 300°C	0	24.1156	0.00
		75	24.1	0.27
	300°C	75	24.1	0.27
		97.5	24.1	0.27
	300°C - 400°C	97.5	24.1	0.27
		142.5	24.1	0.27
	400°C	142.5	24.1	0.27
		165	24.1	0.27
	400°C - 500°C	165	24.1	0.27
		210	24	2.02
	500°C	210	24	2.02
		232.5	23.6	9.02
	500°C - 600°C	232.5	23.6	9.02
		277.5	22	37.01
	600°C	277.5	22	37.01
		300	21.5	45.76
	600°C - 700°C	300	21.5	45.76
		345	20.7	59.76
	700°C	345	20.7	59.76
		367.5	20.6	61.51
32.93	26.9°C - 300°C	0	26.4	0.00
		75	26.4	0.00
	300°C	75	26.4	0.00
		97.5	26.4	0.00
	300°C - 400°C	97.5	26.4	0.00
		142.5	26.4	0.00
	400°C	142.5	26.4	0.00
		165	26.4	0.82
	400°C - 500°C	165	26.4	0.82
		210	26.3	2.50
	500°C	210	26.3	2.50

		232.5	25.8	10.91
	500°C - 600°C	232.5	25.8	10.91
		277.5	25.4	17.63
	600°C	277.5	25.4	17.63
		300	24.4	34.44
	600°C - 700°C	300	24.4	34.44
		345	23.4	51.25
	700°C	345	23.4	51.25
		367.5	23.4	51.25
33.75	26.9°C - 300°C	0	27.74	0.00
		75	27.7	0.55
	300°C	75	27.7	0.55
		97.5	27.7	0.55
	300°C - 400°C	97.5	27.7	0.55
		142.5	27.7	0.55
	400°C	142.5	27.7	0.55
		165	27.5	3.31
	400°C - 500°C	165	27.5	3.31
		210	27.4	4.70
	500°C	210	27.4	4.70
		232.5	27.3	6.08
	500°C - 600°C	232.5	27.3	6.08
		277.5	25.8	26.80
	600°C	277.5	25.8	26.80
		300	24.4	46.13
	600°C - 700°C	300	24.4	46.13
		345	23.9	53.04
	700°C	345	23.9	53.04
		367.5	23.3	53.04
35.64	26.9°C - 300°C	0	25.4437	0.00
		75	25.4437	0.00
	300°C	75	25.4437	0.00
		97.5	25.4437	0.00
	300°C - 400°C	97.5	25.4437	0.00
		142.5	25.4437	0.00
	400°C	142.5	25.4437	0.00
		165	25.4437	0.00

	400°C - 500°C	165	25.4437	0.00
		210	24.6	11.65
	500°C	210	24.6	11.65
		232.5	24	19.93
	500°C - 600°C	232.5	24	19.93
		277.5	23	33.74
	600°C	277.5	23	33.74
		300	22.3	43.40
	600°C - 700°C	300	22.3	43.40
		345	21.8	50.30
	700°C	345	21.8	50.30
		367.5	21.6	53.06
63.23	26.9°C - 300°C	0	30.5514	0.00
		75	30.5	0.53
	300°C	75	30.5	0.53
		97.5	30.5	0.53
	300°C - 400°C	97.5	30.5	0.53
		142.5	30.5	0.53
	400°C	142.5	30.5	0.53
		165	30.5	0.53
	400°C - 500°C	165	30.5	0.53
		210	30.2	3.64
	500°C	210	30.2	3.64
		232.5	29.5	10.89
	500°C - 600°C	232.5	29.5	10.89
		277.5	29	16.07
	600°C	277.5	29	16.07
		300	28.4	22.29
	600°C - 700°C	300	28.4	22.29
		345	28.4	22.29
	700°C	345	28.4	22.29
		367.5	28.4	22.29
65.75	26.9°C - 300°C	0	25.2995	0.00
		75	25.2995	0.00
	300°C	75	25.2995	0.00
		97.5	25.2995	0.00

	300°C - 400°C	97.5	25.2995	0.00
		142.5	25.2995	0.00
	400°C	142.5	25.2995	0.00
		165	25.2995	0.00
	400°C - 500°C	165	25.2995	0.00
		210	25.2	1.49
	500°C	210	25.2	1.49
		232.5	25	1.49
	500°C - 600°C	232.5	25	4.47
		277.5	24.5	11.93
	600°C	277.5	24.5	11.93
		300	24	19.40
	600°C - 700°C	300	24	19.40
		345	24.1	17.90
	700°C	345	24.1	17.90
		367.5	24	19.40

Appendix B

B-1: GCMS Analysis Results

The following data was obtained from the respective online data bases for Tables B.1 – B.17:

- Boiling Point (°C): (Chemspider.com, n.d.)
- Molar Mass (g/mol): (Chemspider.com, n.d.)
- Cp (J/molK): (Chemeo.com, n.d.)
- Hv (kJ/mol): (Chemspider.com, n.d.)

Table B.1: GCMS and Thermodynamic Data for Organic Compounds recovered from Inside the Reactor and Exit tube for 25.69 % Ash Content Coal

Compound Name	Mass %	Boiling Point (°C)	Molar Mass (g/mol)	Cp (J/molK)	(kJ/kg K)	Flowrate (kg/hr)	mCp (kJ/K)	Hv (kJ/mol)	mHv (kJ/kg)	Heat Evolved (kJ)
Propane. 1-(1-ethoxyethoxy)-	17.76	124.8	132.2	242.3	1.83	3.69	6.76	35.50	268.53	-1808.77
Cycloheptane. methyl-	2.96	128.8	112.21	211.56	1.89	0.61	1.16	35.80	319.04	-336.42
Benzene. 1.3-dimethyl-/p-Xylene	2.43	129.6	106.17	190	1.79	0.50	0.90	35.70	336.26	-279.02
Cyclohexane. (2-methylpropyl)-	2.38	171.3	140.27	299.96	2.14	0.49	1.06	39.10	278.76	-265.74
Decane	9.43	171.9	142.28	315.31	2.22	1.96	4.34	38.80	272.70	-1059.43
Phenol	8.56	181.8	94.11	145.52	1.55	1.78	2.75	43.50	462.22	-1154.40
Phenol. 2-methyl-	6.15	191	108.14	184.27	1.70	1.28	2.18	44.50	411.51	-789.02
Undecane	6.88	193.3	156.31	360.07	2.30	1.43	3.29	41.50	265.50	-777.80
p-Cresol	4.77	202	108.14	184.27	1.70	0.99	1.69	45.60	421.68	-622.05
Phenol. 2.4-dimethyl-k	3.62	210.9	122.164	224.69	1.84	0.75	1.38	46.50	380.64	-453.53
Phenol. 3.5-dimethyl-	4.29	211.1	122.16	224.69	1.84	0.89	1.64	47.70	390.46	-546.22
.alpha.-Terpineol/L-.alpha.-Terpineol	2.28	217.5	154.25	454.83	2.95	0.47	1.40	52.80	342.30	-331.10

Naphthalene. 2-methyl-	4.22	236.9	142.20	252.16	1.77	0.88	1.55	45.70	321.39	-469.79
Naphthalene. 1-methyl	2.27	236.9	142.20	252.16	1.77	0.47	0.84	46.00	323.49	-253.70
Tetradecane	2.6	250.9	198.39	505.91	2.55	0.54	1.38	47.10	237.41	-294.89
Naphthalene. 2.6-dimethyl-	1.57	254.4	156.224	296.31	1.90	0.33	0.62	48.20	308.53	-175.46
Anthracene	2.01	328.4	178.229	334.16	1.87	0.42	0.78	55.80	313.08	-225.43
Unknown 1	0.45									
Unknown 2	11.4									
Unknown 3	2									
Unknown 4	1.98									

Table B.2: GCMS and Thermodynamic Data for Organic Compounds in the of Organic Fraction, recovered Externally for 25.69 % Ash Content Coal

Compound Name	Mass %	Boiling Point (°C)	Molar Mass (g/mol)	Cp (J/molK)	(kJ/kgK)	Flowrate (kg/hr)	mCp (kJ/K)	Hv (kJ/mol)	mHv (kJ/kg)	Heat Evolved (kJ)
p-Xylene/o-Xylene	8.5	129.6	106.17	211.09	1.99	0.21	0.41	35.70	336.26	-118.93
Benzene. 1.3-dimethyl- /p-Xylene	0.44	129.6	106.167	190	1.79	0.19	0.33	35.70	336.26	-102.58
Pyridine. 2.4-dimethyl-	13.02	148.4	107.15	185.17	1.73	0.18	0.31	38.50	359.31	-101.85
Benzene. 1.2.3-trimethyl-	1.57	156.8	120.19	216.81	1.80	0.19	0.34	39.60	329.48	-102.45
Benzene. 1-propenyl-	1.12	167.5	118.18	199.03	1.68	0.17	0.29	38.70	327.47	-92.77
Phenol	0.69	181.8	94.111	145.52	1.55	0.16	0.25	43.50	462.22	-104.10
1H-Indene. 1.1-dimethyl-	2.35	186.5	144.213	270.35	1.87	0.19	0.36	42.50	294.70	-101.38
Phenol. 2-methyl-	0.43	191	108.138	184.27	1.70	0.18	0.30	44.50	411.51	-109.14
Phenol. 2.6-dimethyl-	1.59	201.1	122.164	224.69	1.84	0.19	0.35	45.50	372.45	-113.47
Phenol. 3-methyl-	4.71	202.3	108.06	184.27	1.71	0.18	0.30	45.60	421.99	-111.09
Phenol. 2-ethyl-4-methyl-	1.13	205.9	136.19	267.07	1.96	0.20	0.40	47.00	345.11	-118.42
Phenol. 2.4-dimethyl-/Phenol. 2.5-dimethyl-	11.96	211.1	122.16	224.69	1.84	0.19	0.35	46.50	380.64	-115.03
Azulene /Naphthalene	4.03	214.5	128.171	209.58	1.64	0.17	0.28	43.90	342.51	-91.62

Phenol. 2.3.6-trimethyl-/Phenol. 2.3.5-trimethyl-	2.04	222.1	136.191	266.77	1.96	0.20	0.40	47.80	350.98	-119.43
Phenol. 3-ethyl-5-methyl-	2.38	223.8	136.19	266.77	1.96	0.20	0.40	48.90	359.06	-121.07
Phenol. 3-(1-methylethyl)-	3.53	228	136.19	267.53	1.96	0.20	0.40	48.30	354.65	-120.65
Phenol. 2-methyl-5-(1-methylethyl)-	2.3	228.2	150.1	311.65	2.08	0.22	0.45	49.30	328.45	-124.80
Naphthalene. 2-methyl-	3.86	236.9	142.197	252.16	1.77	0.18	0.33	45.70	321.39	-98.55
Naphthalene. 1.3-dimethyl-	2.6	253.7	156.224	296.31	1.90	0.20	0.37	48.10	307.89	-105.69
Naphthalene. 2.3.6-trimethyl-	2.83	263.5	170.25	342	2.01	0.21	0.42	48.10	282.53	-109.48
Dodecyl acrylate	2.09	295.2	240.38	598.68	2.49	0.26	0.64	54.70	227.56	-136.61
Unknown 1	15.5									
Unknown 2	7.6									
Unknown 3	2.13									
Unknown 4	1.6									

Table B.3: GCMS and Thermodynamic Data for of Organic compounds in the Aqueous Fraction, recovered Externally for 25.69 % Ash Content Coal

Compound Name	Mass %	Boiling Point (°C)	Molar Mass (g/mol)	Cp (J/molK)	(kJ/kg K)	Flowrate (kg/hr)	mCp (kJ/K)	Hv (kJ/mol)	mHv (kJ/kg)	Heat Evolved (kJ)
Propane. 1.1-diethoxy-	3.53	122.8	132.201	242.3	1.83	0.03	0.06	34.60	261.72	-16.22
Propanoic acid	1.21	138.7	74.078	163.46	2.21	0.04	0.09	40.10	541.32	-32.64
Cyclohexane. (2-methylpropyl)-	1.94	171.3	140.266	299.96	2.14	0.04	0.08	39.10	278.76	-21.03
Decane	2.88	171.9	142.282	315.31	2.22	0.04	0.09	38.80	272.70	-21.93
Phenol	1.15	181.8	94.111	145.52	1.55	0.03	0.04	43.50	462.22	-18.37
Phenol. 3-methyl-	6.15	191	108.138	184.27	1.70	0.03	0.05	45.60	421.68	-19.58
Phenol. 2.4-dimethyl-	1.23	210.9	122.164	224.69	1.84	0.03	0.06	46.50	380.64	-20.30
Phenol. 2.5-dimethyl-	4.72	211.1	122.16	224.69	1.84	0.03	0.06	46.60	381.45	-20.33
Phenol. 2.3-dimethyl-	3.64	216.9	122.164	224.69	1.84	0.03	0.06	47.20	386.37	-20.49
L-.alpha.-Terpineol	1.18	217.5	154.249	454.83	2.95	0.05	0.16	52.80	342.30	-37.72
Tridecane	1.1	231.5	184.36	455.48	2.47	0.05	0.11	45.20	245.17	-24.60
Unknown 1	21.01									
Unknown 2	15.96									
Unknown 3	15.1									
Unknown 4	6.99									

Unknown 5	3.42									
Unknown 6	2.93									
Unknown 7	2.91									
Unknown 8	2.07									
Unknown 9	0.88									

Table B.4: GCMS and Thermodynamic Data for Organic Compounds recovered from Inside the Reactor and Exit tube for 32.93 % Ash Content Coal

Compound Name	Mass %	Boiling Point (°C)	Molar Mass (g/mol)	Cp (J/molK)	(kJ/kg K)	Flowrate (kg/hr)	mCp (kJ/K)	Hv (kJ/mol)	mHv (kJ/kg)	Heat Evolved (kJ)
Propane. 1.1-diethoxy-	25.12	122.8	132.20	242.3	1.83	4.95	9.07	34.60	142.80	-1970.74
p-Xylene	3.21	129.6	106.17	211.09	1.99	0.63	1.26	35.70	169.12	-282.18
Nonane	3.22	148.7	128.26	272.69	2.13	0.63	1.35	36.90	135.32	-273.81
Octane. 2.3-dimethyl-	4.54	157.5	142.28	315.26	2.22	0.89	1.98	38.50	122.12	-385.43
Cyclohexane. (2-methylpropyl)-	14.46	171.3	140.27	299.96	2.14	2.85	6.09	39.10	130.35	-1220.36
Decane	6.48	171.9	142.28	315.31	2.22	1.28	2.83	38.80	123.05	-551.37
Undecane	4.64	193.3	156.31	360.07	2.30	0.91	2.11	41.50	115.26	-398.83
p-Cresol	2.17	202	108.14	267.07	2.47	0.43	1.06	45.60	170.74	-220.14
.alpha.-Terpineol	1.94	217.5	154.25	454.3	2.95	0.38	1.13	52.80	116.22	-201.30
Naphthalene. 2-methyl-	2.49	236.9	142.20	252.16	1.77	0.49	0.87	45.70	181.23	-210.13
Tetradecane	3.82	250.9	198.39	505.91	2.55	0.75	1.92	47.10	93.10	-337.54
Naphthalene. 1.2-dimethyl-	2.11	258.9	156.22	296.31	1.90	0.42	0.79	48.70	164.35	-178.20
Naphthalene. 2.3.6-trimethyl-	4.66	263.5	170.25	342	2.01	0.92	1.84	48.10	140.64	-386.13
Dibenzofuran	2.12	285	168.19	199.01	1.18	0.42	0.49	50.50	253.76	-174.84

9H-Fluorene. 1-methyl-	2.11	296.5	180.25	352.92	1.96	0.42	0.81	53.50	151.59	-176.44
[1.1'-Biphenyl]-4-carboxaldehyde	1.11	305.6	182.218	342.32	1.88	0.22	0.41	56.90	166.22	-93.60
Anthracene	3.75	328.4	178.229	334.16	1.87	0.74	1.38	55.80	166.99	-316.40
9H-Fluoren-9-ol	0.58	356.5	182.218	357.87	1.96	0.11	0.22	64.80	181.07	-51.96
Unknown 1	9.74									0.00
Unknown 2	1.71									

Table B.5: GCMS and Thermodynamic Data for Organic Compounds in the of Organic Fraction, recovered Externally for 32.93 % Ash Content Coal

Compound Name	Mass %	Boiling Point (°C)	Cp (J/molK)	(kJ/kg K)	Flowrate (kg/hr)	mCp (kJ/K)	Hv (kJ/mol)	mHv (kJ/kg)	Heat Evolved (kJ)
Phenol	17.21	181.8	145.52	1.55	1.69	2.62	43.50	298.93	-870.62
Phenol. 2-methyl-	24.91	191	184.27	1.70	2.45	4.17	44.50	241.49	-1173.34
Phenol. 2.6-dimethyl-	1.89	201.1	224.69	1.84	0.19	0.34	46.60	207.40	-86.19
Phenol. 3-ethyl- /Phenol. 2-ethyl-	0.87	202.7	224.79	1.84	0.09	0.16	46.60	207.30	-39.68
1H-Imidazole. 1.2-dimethyl-	2.11	206.6	224.79	2.34	0.21	0.49	42.40	188.62	-106.77
Phenol. 2.5-dimethyl-	10.83	211.1	224.69	1.84	1.06	1.96	46.60	207.40	-493.89
Phenol. 3.4-dimethyl-	2.54	211.1	224.69	1.84	0.25	0.46	48.20	214.52	-117.61
Naphthalene	4.56	214.5	209.58	1.64	0.45	0.73	43.90	209.47	-196.13
Phenol. 2.3.5-trimethyl-	0.53	222.1	266.77	1.96	0.05	0.10	48.70	182.55	-23.74
Naphthalene. 2-methyl-	5.4	236.9	252.16	1.77	0.53	0.94	45.70	181.23	-227.49
1.1'-Biphenyl. 2-methyl-	1.32	248	324.5	1.93	0.13	0.25	47.60	146.69	-53.94
Naphthalene. 1.3-dimethyl-	5.01	253.7	296.31	1.90	0.49	0.93	48.10	162.33	-210.22
Naphthalene. 2.3-dimethyl-	1.01	258.9	296.31	1.90	0.10	0.19	48.70	164.35	-42.58
Naphthalene. 2.3.6-trimethyl-	3.52	263.5	342	2.01	0.35	0.70	48.10	140.64	-145.60
Naphthalene. 1-methyl-7-(1-methylethyl)-	1.36	274.2	390.19	2.12	0.13	0.28	50.20	128.66	-56.68
Dibenzofuran	1.34	285	199.01	1.18	0.13	0.16	50.50	253.76	-55.17

[1.1'-Biphenyl]-4-carboxaldehyde	1.96	305.6	342.32	1.88	0.19	0.36	56.90	166.22	-82.51
9H-Fluorene. 2-methyl-	1.48	318	352.92	1.96	0.15	0.28	53.70	152.16	-61.87
Anthracene	3.11	328.4	334.16	1.87	0.31	0.57	55.80	166.99	-130.99
Anthracene. 9-methyl-	2.12	347.2	381.22	1.98	0.21	0.41	56.80	149.00	-88.68
9.10-Dimethylanthracene	1.57	358.8	429.69	2.08	0.15	0.32	59.40	138.24	-66.17
Unknown 1	0.86								
Unknown 2	1.45								
Unknown 3	0.55								
Unknown 4	1.2								
Unknown 5	1.26								

Table B.6: GCMS and Thermodynamic Data for of Organic compounds in the Aqueous Fraction, recovered Externally for 32.93 % Ash Content Coal

Compound Name	Mass %	Boiling Point (°C)	Cp (J/molK)	(kJ/kg K)	Flowrate (kg/hr)	mCp (kJ/K)	Hv (kJ/mol)	mHv (kJ/kg)	Heat Evolved (kJ)
Acetamide	2.1	55.4	85.13	1.44	0.04	0.05	37.20	436.98	-23.25
Propanamide	1.69	80	117.4	1.61	0.03	0.05	39.90	339.86	-16.54
2-Propanone. dimethylhydrazone	3.28	87	77.89	0.78	0.06	0.04	34.90	448.07	-31.67
Acetic acid	1.14	114.1	77.89	1.30	0.02	0.03	23.70	304.28	-9.60
Propanoic acid	4.84	138.7	163.46	2.21	0.08	0.19	40.10	245.32	-46.44
1H-Pyrazole. 1.3.5-trimethyl-	3.15	150.1	163.46	1.48	0.05	0.08	37.90	231.86	-23.98
Pyrazine. 2.5-diethyl-	0.84	155.7	163.46	1.20	0.01	0.02	40.90	250.21	-6.09
Pyridine. 2.4.6-trimethyl-	3.64	162	215.1	1.78	0.06	0.11	39.90	185.50	-27.36
2-(Diethylamino)acetonitrile	0.83	170	219.83	1.96	0.01	0.03	40.60	184.69	-6.59
Pyridine. 2-ethyl-4.6-dimethyl-	0.57	177.3	219.32	1.62	0.01	0.02	40.50	184.66	-4.06
Phenol	2.04	181.8	145.52	1.19	0.04	0.04	43.50	298.93	-16.46
Phenol. 2-methyl-	24.82	191	184.27	1.70	0.43	0.73	44.50	241.49	-206.31
Cyclohexanol. 3.3.5-trimethyl-. acetate. cis-	3.29	201.8	404.89	2.20	0.06	0.13	44.60	110.15	-23.77
1H-Imidazole. 1.2-dimethyl-	6.58	206	219.83	2.29	0.11	0.26	42.40	192.88	-58.42
1H-Imidazole. 2-ethyl-4-methyl-	23.77	293.5	219.83	2.00	0.41	0.82	51.20	232.91	-210.81
Unknown 1	15.26								

Unknown 2	0.74								
Unknown 3	0.73								
Unknown 4	0.7								

Table B.7: GCMS and Thermodynamic Data for Organic Compounds recovered from Inside the Reactor and Exit tube for 33.75 % Ash Content Coal

Compound Name	Mass %	Boiling Point (°C)	Molar Mass (g/mol)	Cp (J/molK)	(kJ/kg K)	Flowrate (kg/hr)	mCp (kJ/K)	Hv (kJ/mol)	mHv (kJ/kg)	Heat Evolved (kJ)
Propane. 1.1-diethoxy-	12.93	122.8	132.20	242.30	1.83	2.13	3.91	34.60	142.80	-502.18
Benzene. 1.3-dimethyl-/p-Xylene	1.51	130.6	106.17	190.00	1.79	0.25	0.45	35.70	187.89	-69.35
Nonane. 4-methyl-	5.34	159.1	142.28	315.29	2.22	0.88	1.95	38.60	122.43	-206.48
Cyclohexane. (2-methylpropyl)-	5.36	171.3	140.27	299.96	2.14	0.88	1.89	39.10	130.35	-210.80
Phenol	0.85	181.8	94.111	145.52	1.55	0.14	0.22	43.5	298.93	-52.89
Phenol. 2-methyl-	3.8	191	108.14	184.27	1.70	0.63	1.07	44.50	241.49	-205.43
Undecane	12.44	193.3	156.31	360.07	2.30	2.05	4.73	41.50	115.26	-475.35
Benzene. 1-ethyl-4-methoxy-	2.56	195.5	136.19	224.69	1.65	0.42	0.70	41.40	184.25	-113.05
Phenol. 2.6-dimethyl-	1.46	201.1	122.164	224.69	1.84	0.24	0.44	45.5	202.50	-71.17
p-Cresol	6.08	202	108.14	267.07	2.47	1.00	2.48	45.60	170.74	-296.43
Phenol. 2-ethyl-	11.04	202.7	122.16	224.79	1.84	1.82	3.35	45.90	204.19	-541.34
Phenol. 2-ethyl-4-methyl-	2.6	205.9	136.19	267.07	1.96	0.43	0.84	47.00	175.98	-118.00
Phenol. 2.5-dimethyl-	0.7	211.1	122.164	224.69	1.84	0.12	0.21	46.6	207.40	-34.69

.alpha.-Terpineol	9.58	217.5	154.25	454.83	2.95	1.58	4.66	52.80	116.09	-418.85
Phenol. 3-(1-methylethyl)-	2.17	228	136.19	267.53	1.96	0.36	0.70	43.80	163.72	-94.15
Naphthalene. 2-methyl-	3.02	236.9	142.20	252.16	1.77	0.50	0.88	45.70	181.23	-134.96
Tetradecane	1.2	250.9	198.388	505.91	2.55	0.20	0.51	47.1	93.10	-43.93
Octadecane/Hexadecane	2.51	311.3	254.49	723.50	2.84	0.41	1.18	53.50	73.95	-90.07
Unknown 1	6.93									
Unknown 2	2.71									
Unknown 3	1.92									
Unknown 4	1.89									
Unkown 5	1.41									

Table B.8: GCMS and Thermodynamic Data for Organic Compounds in the of Organic Fraction, recovered Externally for 33.75 % Ash Content Coal

Compound Name	Mass %	Boiling Point (°C)	Molar Mass (g/mol)	Cp (J/molK)	(kJ/kgK)	Flowrate (kg/hr)	mCp (kJ/K)	Hv (kJ/mol)	mHv (kJ/kg)	Heat Evolved (kJ)
Phenol	0.76	181.8	94.111	145.52	1.55	0.08	0.12	43.50	298.93	-30.24
Phenol. 2-methyl-	0.39	191	108.138	184.27	1.70	0.04	0.07	45.60	247.46	-13.73
p-Cresol	9.76	202	108.138	267.07	2.47	1.03	2.54	35.70	133.67	-266.05
Benzene. 1.3-dimethyl-	10.12	130.6	106.165	190	1.79	1.07	1.91	38.50	202.63	-312.88
Pyridine. 2.4-dimethyl-	21.47	148.4	107.15	184.76	1.72	2.27	3.91	38.50	208.38	-669.33
Phenol. 2.6-dimethyl-	1.3	201.1	122.164	224.69	1.84	0.14	0.25	45.50	202.50	-40.52
Phenol.2-ethyl-	1.49	202.7	122.164	224.79	1.84	0.16	0.29	45.90	204.19	-46.71
Phenol. 2.4-dimethyl-	14.3	201.1	122.164	224.69	1.84	1.51	2.78	46.50	206.95	-452.40
Phenol. 3-ethyl-	10.75	202.7	122.164	224.79	1.84	1.13	2.09	46.60	207.30	-340.54
Phenol. 3.4-dimethyl-	2.79	211.1	122.164	224.69	1.84	0.29	0.54	48.20	214.52	-90.49
Phenol. 2.3.6-trimethyl-	5.82	177	121.18	266.77	2.20	0.61	1.35	47.80	179.18	-178.29
Phenol. 3-(1-methylethyl)-	2.61	228	136.19	267.53	1.96	0.28	0.54	48.30	180.54	-77.03
Benzene. 1-ethyl-4-methoxy-	4.21	195.5	136.19	239.26	1.76	0.44	0.78	41.40	173.03	-116.27
Phenol. 2-ethyl-4-methyl-	2.78	205.9	136.191	267.07	1.96	0.29	0.58	47.00	175.98	-80.67
Phenol. 2-methyl-5-(1-methylethyl)-	0.45	228.2	150.1	311.65	2.08	0.05	0.10	49.30	158.19	-12.49

1.5-Diydroxy-1.2.3.4-tetrahydronaphthalene	1.19	325.9	164.2	311.65	1.90	0.13	0.24	49.30	158.19	-31.90
1H-Inden-5-ol. 2.3-dihydro-	1.38	253	134.18	250.4	1.87	0.15	0.27	51.00	203.67	-43.38
Phenol. 2.3.5.6-tetramethyl-	2.09	239	150.22	310.51	2.07	0.22	0.46	50.50	162.64	-58.88
Naphthalene. 2.3-dimethyl-	1.41	258.9	156.224	296.31	1.90	0.15	0.28	48.70	164.35	-38.70
Naphthalene. 2.3.6-trimethyl-	2.68	263.5	170.25	342	2.01	0.28	0.57	48.10	140.64	-68.45
1-Naphthalenol. 2-methyl-	1.54	236.9	142.197	296.31	2.08	0.16	0.34	56.60	191.02	-48.14
[1.1'-Biphenyl]-4-carboxaldehyde	1.74	305.6	182.218	342.32	1.88	0.18	0.35	56.90	166.22	-47.93
Unknown 1	1.12									

Table B.9: GCMS and Thermodynamic Data for Organic Compounds recovered from Inside the Reactor and Exit tube for 35.64 % Ash Content Coal

Compound Name	Mass %	Boiling Point (°C)	Molar Mass (g/mol)	Cp (J/mol K)	(kJ/kgK)	Flowrate (kg/hr)	mCp (kJ/K)	Hv (kJ/mol)	mHv (kJ/kg)	Heat Evolved (kJ)
Propane. 1-(1-ethoxyethoxy)-	17.77	124.8	132.20	242.3	0.55	2.59	1.41	35.50	146.51	-539.81
Benzene. 1.3-dimethyl-	2.43	130.6	106.17	190	0.56	0.35	0.20	35.70	187.89	-88.98
Cyclohexane. 1-ethyl-4-methyl-. trans- /Cyclohexane. 1-ethyl-4-methyl-. cis-	2.61	143.8	126.24	255.07	0.49	0.38	0.19	37.20	145.84	-76.84
Nonane. 4-methyl-	2.32	159.1	142.28	315.29	0.45	0.34	0.15	38.60	122.43	-58.71
Cyclohexane. (2-methylpropyl)-	7.4	171.3	140.27	299.96	0.47	1.08	0.50	39.10	130.35	-197.81
Decane	4.64	171.9	142.28	315.31	0.45	0.68	0.30	38.80	123.05	-117.84
Benzofuran. 2.3-dihydro-	0.63	178.2	120.148	187.41	0.64	0.09	0.06	40.70	217.17	-26.62
Phenol	4.25	181.8	94.11	145.52	0.65	0.62	0.40	43.50	298.93	-230.52
Phenol. 2-methyl-	15.27	191	108.14	184.27	0.59	2.22	1.30	44.50	241.49	-685.42
Undecane	1.61	193.3	156.31	360.07	0.43	0.23	0.10	41.50	115.26	-38.60
Phenol. 3-ethyl- /Phenol. 2-ethyl-	4.57	202.7	122.16	224.79	0.54	0.67	0.36	46.60	207.30	-179.10
Phenol. 2.4-dimethyl-	6.62	210.9	122.16	224.69	0.54	0.96	0.52	46.50	206.95	-259.13

.alpha.-Terpineol	10.49	217.5	154.25	224.69	0.69	1.53	1.05	52.80	234.99	-478.28
Phenol. 3-ethyl-5-methyl-	0.7	223.8	136.19	266.77	0.51	0.10	0.05	48.90	183.30	-24.61
Naphthalene. 2-methyl-	5.18	236.9	142.20	252.16	0.56	0.75	0.43	45.70	181.23	-185.11
2-Propenal. 3-phenyl-	1.26	237.8	132.16	217.59	0.61	0.18	0.11	48.40	222.44	-53.49
Tetradecane	1.73	250.9	198.39	505.91	0.39	0.25	0.10	47.10	93.10	-34.70
Naphthalene. 1.3-dimethyl-/ Naphthalene. 1.8-dimethyl-	2.28	253.7	156.22	296.31	0.53	0.33	0.17	48.10	162.33	-73.82
Naphthalene. 1.6-dimethyl-/Naphthalene. 2.6-dimethyl-	0.58	254.4	156.224	296.31	0.53	0.08	0.04	48.20	162.67	-18.81
Phenanthrene/Anthracene	3.35	328.4	178.23	334.16	0.53	0.49	0.26	55.80	166.99	-111.07
Unknown 1	2.39									
Unknown 2	1.91									

Table B.10: GCMS and Thermodynamic Data for Organic Compounds in the of Organic Fraction, recovered Externally for 35.64 % Ash Content Coal

Compound Name	Mass %	Boiling Point (°C)	Molar Mass (g/mol)	Cp (J/molK)	(kJ/kgK)	Flowrate (kg/hr)	mCp (kJ/K)	Hv (kJ/mol)	mHv (kJ/kg)	Heat Evolved (kJ)
p-Xylene/o-Xylene	0.49	129.6	106.167	211.09	1.99	0.06	0.11	35.70	169.12	-22.15
Benzene. 1.3-dimethyl-	0.5	130.6	106.165	190	1.79	0.06	0.10	35.70	187.89	-22.38
Benzene. 1.2.3-trimethyl- /Benzene. 1.2.4-trimethyl-	0.99	156.8	120.192	216.81	1.80	0.11	0.20	39.60	182.65	-43.90
Phenol	5.93	181.8	94.111	145.52	1.55	0.68	1.05	43.50	298.93	-321.81
1H-Indene. 1.1-dimethyl-	2.36	186.5	144.213	270.35	1.87	0.27	0.51	42.50	157.20	-99.96
Phenol. 2-methyl-	24.71	191	108.138	184.27	1.70	2.82	4.81	44.50	241.49	-1229.63
Phenol. 2.6-dimethyl-	15.71	201.1	122.164	224.69	1.84	1.79	3.30	45.50	202.50	-739.47
Phenol. 3-ethyl-	6.82	202.7	122.164	224.79	1.84	0.78	1.43	46.60	207.30	-324.83
Naphthalene	3.08	214.5	128.171	226.7	1.77	0.35	0.62	43.90	193.65	-139.03
Phenol. 2-(1-methylethyl)-/Phenol. 4-(1-methylethyl)-	2.04	228	136.19	267.53	1.96	0.23	0.46	46.80	174.93	-92.92
Naphthalene. 2-methyl- /Naphthalene. 1-methyl-	1.28	236.9	142.197	252.16	1.77	0.15	0.26	45.70	181.23	-56.04
Naphthalene. 1-methyl-	1	239.8	142.197	252.16	1.77	0.11	0.20	46.00	182.42	-43.92

1H-Inden-1-one. 2.3-dihydro-3.3-dimethyl-	2.64	240.8	160.21	252.16	1.57	0.30	0.47	48.80	193.53	-112.44
Naphthalene. 2.6-dimethyl-	4.54	254.4	156.224	296.31	1.90	0.52	0.98	48.20	162.67	-196.44
Naphthalene. 2.3-dimethyl-	0.64	258.9	156.224	296.31	1.90	0.07	0.14	48.70	164.35	-27.82
Naphthalene. 2.3.6-trimethyl-	2.42	263.5	170.25	342	2.01	0.28	0.56	48.10	140.64	-102.16
3.5.3'.5'-Tetramethylbiphenyl	0.6	263.9	210.31	342	1.63	0.07	0.11	51.90	151.75	-23.10
1-Pentadecene	1.69	265.7	210.4	537.93	2.56	0.19	0.49	48.60	90.35	-73.69
Pentadecane	1.62	267.6	212.42	558.03	2.63	0.19	0.49	48.80	87.45	-71.58
Heptadecane	0.69	296.8	240.47	666.92	2.77	0.08	0.22	52.00	77.97	-31.06
[1.1'-Biphenyl]-4-carboxaldehyde	1.24	305.6	182.218	342.32	1.88	0.14	0.27	56.90	166.22	-53.86
Octadecane /Heneicosane	2.96	311.3	254.49	723.5	2.84	0.34	0.96	53.50	73.95	-134.55
Nonadecane	0.95	325.1	268.52	781.39	2.91	0.11	0.32	55.00	70.39	-43.63
Anthracene	1.34	328.4	178.229	334.16	1.87	0.15	0.29	55.80	166.99	-58.26
Phenanthrene. 1-methyl-	0.81	344.5	192.26	381.22	1.98	0.09	0.18	57.50	150.83	-34.86
9H-Fluoren-9-ol	2.13	356.5	182.218	357.87	1.96	0.24	0.48	64.80	181.07	-98.50
9.10-Dimethylanthracene	0.74	358.8	206.28	429.69	2.08	0.08	0.18	59.40	138.24	-31.75
Unknown 1	2.69									
Unknown 2	1.99									
Unknown 3	1.2									
Unknown 4	1.17									
Unknown 5	1.13									

Unknown 6	1.12									
Unknown 7	0.76									

Table B.11: GCMS and Thermodynamic Data for Organic compounds in the Aqueous Fraction, recovered Externally for 35.64 % Ash Content Coal

Compound Name	Mass %	Boiling Point (°C)	Molar Mass (g/mol)	Cp (J/molK)	(kJ/kg K)	Flowrate (kg/hr)	mCp (kJ/K)	Hv (kJ/mol)	mHv (kJ/kg)	Heat Evolved (kJ)
2-Propanone. dimethylhydrazone	0.77	87	100.162	242.3	2.42	0.02	0.04	34.90	144.04	-6.51
Propane. 1.1-diethoxy-	2.16	122.8	132.201	242.3	1.83	0.04	0.08	34.60	142.80	-15.31
Propanoic acid	0.68	138.7	74.078	238.65	3.22	0.01	0.04	40.10	168.03	-7.34
Butanoic acid	1.51	161.3	88.105	146.1	1.66	0.03	0.05	42.40	290.21	-14.58
Cyclohexane. (2-methylpropyl)-	1.46	171.3	140.266	299.96	2.14	0.03	0.06	39.10	130.35	-11.01
Decane	1	171.9	142.282	315.31	2.22	0.02	0.04	38.80	123.05	-7.57
Phenol	31.76	181.8	94.111	145.52	1.55	0.64	0.99	43.50	298.93	-304.15
Phenol. 2-methyl-	35.84	191	108.138	184.27	1.70	0.72	1.23	44.50	241.49	-314.73
Benzene. 1-ethyl-4-methoxy-	0.78	195.5	136.19	184.27	1.35	0.02	0.02	41.40	224.67	-5.96
Phenol. 2.6-dimethyl-	0.93	201.1	122.164	224.69	1.84	0.02	0.03	45.50	202.50	-7.72
Phenol. 3-ethyl-	0.65	202.7	122.164	224.79	1.84	0.01	0.02	46.60	207.30	-5.46
Phenol. 2.4-dimethyl-	6.37	210.9	122.164	224.69	1.84	0.13	0.24	46.50	206.95	-53.48
Phenol. 2.3-dimethyl-	4.22	216.9	122.164	224.69	1.84	0.09	0.16	47.20	210.07	-35.70
Catechol	5.49	245.5	110.11	186.33	1.69	0.11	0.19	50.20	269.41	-51.15
Tetradecane	0.84	250.9	198.388	505.91	2.55	0.02	0.04	47.10	93.10	-6.50

Unknown 1	1.86									
Unknown 2	1.44									
Unknown 3	0.85									
Unknown 4	0.73									
Unknown 5	0.64									

Table B.12: GCMS and Thermodynamic Data for Organic Compounds recovered from Inside the Reactor and Exit tube for 63.23 % Ash Content Coal

Compound Name	Mass %	Boiling Point (°C)	Molar Mass (g/mol)	Cp (J/molK)	(kJ/kgK)	Flowrate (kg/hr)	mCp (kJ/K)	Hv (kJ/mol)	mHv (kJ/kg)	Heat Evolved (kJ)
Propane. 1.1-diethoxy-	3.84	122.8	132.20	242.3	1.83	0.40	0.74	34.60	261.72	-210.15
Benzene. 1.3-dimethyl-	23.35	130.6	106.17	190	1.79	2.44	4.37	35.70	336.27	-1444.87
Cyclohexane. 1-ethyl-4-methyl-. trans-	2.55	143.8	126.24	255.07	2.02	0.27	0.54	37.20	294.68	-155.49
Nonane. 2-methyl-	3.03	163.9	142.28	315.29	2.22	0.32	0.70	38.20	268.48	-185.29
Cyclohexane. (2-methylpropyl)-	3.16	171.3	140.27	299.96	2.14	0.33	0.71	39.10	278.76	-192.98
Decane	0.88	171.9	142.28	315.31	2.22	0.09	0.20	38.80	272.70	-54.20
Phenol	9.95	181.8	94.11	145.52	1.55	1.04	1.61	43.50	462.22	-710.61
Phenol. 2-methyl-	2.82	191	108.14	184.27	1.70	0.29	0.50	44.50	411.51	-193.08
Undecane	0.94	193.3	156.31	360.07	2.30	0.10	0.23	41.50	265.50	-58.42
p-Cresol	5.73	202	108.14	184.27	1.70	0.60	1.02	45.60	421.68	-398.43
Phenol. 2.5-dimethyl-	2.88	211.1	122.16	224.69	1.84	0.30	0.55	46.60	381.45	-193.95
Phenol. 2.3-dimethyl-	1.14	216.9	122.16	224.69	1.84	0.12	0.22	47.20	386.37	-77.36
L-.alpha.-Terpineol/.alpha.-Terpineol	3.26	217.5	154.25	224.69	1.46	0.34	0.50	52.80	342.30	-187.58

Naphthalene. 2-methyl-	11.36	236.9	142.20	252.16	1.77	1.19	2.11	45.70	321.39	-682.49
Tetradecane	1.47	250.9	198.39	505.91	2.55	0.15	0.39	47.10	237.41	-92.45
Naphthalene. 2.3-dimethyl-	5.29	258.9	156.22	296.31	1.90	0.55	1.05	48.70	311.73	-322.22
Hexadecane	3.13	283.6	226.44	611.73	2.70	0.33	0.88	50.50	223.02	-199.21
Phenanthrene/9H-Fluorene. 9-methylene-	4.56	328.4	178.23	334.16	1.87	0.48	0.89	52.50	294.56	-268.08
Unknown 1	3.84									
Unknown 2	2.97									
Unknown 3	2.33									
Unknown 4	1.52					0.16				

Table B.13: GCMS and Thermodynamic Data for Organic Compounds in the of Organic Fraction, recovered Externally for 63.23 % Ash Content Coal

Compound Name	Mass %	Boiling Point (°C)	Molar Mass (g/mol)	Cp (J/molK)	(kJ/kg K)	Flowrate (kg/hr)	mCp (kJ/K)	Hv (kJ/mol)	mHv (kJ/kg)	Heat Evolved (kJ)
Pyridine. 2.6-dimethyl-	0.36	144	107.153	185.17	1.73	0.02	0.04	37.50	349.97	-12.73
Benzene. 1.2.3-trimethyl-	1.25	156.8	120.192	216.81	1.80	0.07	0.13	39.60	329.47	-43.48
Pyridine. 3.5-dimethyl-	0.54	161.7	107.153	216.81	2.02	0.03	0.06	39.50	368.63	-21.04
Benzene. 4-ethyl-1.2-dimethyl-	1.92	169.7	134.218	258.11	1.92	0.11	0.22	40.90	304.73	-65.90
Phenol	3.98	181.8	94.111	145.52	1.55	0.24	0.36	43.50	462.22	-161.07
1H-Indene. 1.1-dimethyl-	4.63	186.5	144.213	270.35	1.87	0.27	0.51	42.50	294.70	-154.27
Phenol. 2-methyl-	19.79	191	108.138	184.27	1.70	1.17	2.00	44.50	411.51	-767.84
Phenol. 2.6-dimethyl-	1.4	201.1	122.164	224.69	1.84	0.08	0.15	45.50	372.45	-52.68
Phenol. 3-ethyl-	12.98	202.7	122.164	224.69	1.84	0.77	1.41	46.60	381.45	-495.34
Phenol. 2-ethyl-4-methyl-	1.06	205.9	136.191	267.07	1.96	0.06	0.12	47.00	345.10	-39.26
Phenol. 2.4.6-trimethyl-	1.74	206.8	136.191	266.77	1.96	0.10	0.20	47.10	345.84	-64.49
Phenol. 2.4-dimethyl-	0.78	210.9	122.164	224.69	1.84	0.05	0.09	46.50	380.64	-29.73
Naphthalene	5.1	214.5	128.171	226.7	1.77	0.30	0.53	43.90	342.51	-179.81

Phenol. 2.3-dimethyl-	5.95	216.9	122.164	224.69	1.84	0.35	0.65	47.20	386.37	-228.79
Phenol. 2.3.5-trimethyl-	3.15	222.1	136.191	266.77	1.96	0.19	0.37	48.70	357.59	-118.94
Phenol. 3-ethyl-5-methyl-	2.61	223.8	136.191	266.77	1.96	0.15	0.30	48.90	359.05	-98.78
Thymol	4.37	233	150.218	311.65	2.07	0.26	0.54	48.90	325.53	-160.98
Naphthalene. 2-methyl-	2.26	236.9	142.197	252.16	1.77	0.13	0.24	45.70	321.39	-76.94
Naphthalene. 1-methyl-	1.65	239.8	142.197	252.16	1.77	0.10	0.17	46.00	323.49	-56.38
1.1'-Biphenyl. 2-methyl-	2.76	248	168.234	324.5	1.93	0.16	0.32	47.60	282.94	-91.31
Naphthalene. 1.3-dimethyl-	1.69	253.7	156.224	296.31	1.90	0.10	0.19	48.10	307.89	-57.95
Naphthalene. 2.6-dimethyl-	4.54	254.4	156.224	296.31	1.90	0.27	0.51	48.20	308.53	-155.84
Naphthalene. 2.3.6-trimethyl-	3.42	263.5	170.25	342	2.01	0.20	0.41	48.10	282.53	-115.37
Fluorene	1.6	283.6	166.219	306.8	1.85	0.09	0.18	51.20	308.03	-54.18
[1.1'-Biphenyl]-4-carboxaldehyde	3.48	305.6	182.218	342.32	1.88	0.21	0.39	56.90	312.26	-119.69
9H-Fluorene. 2-methyl-	0.56	318	180.245	352.92	1.96	0.03	0.06	53.70	297.93	-19.16
Anthracene	0.7	328.4	178.229	334.16	1.87	0.04	0.08	55.80	313.08	-24.09
9H-Fluoren-9-ol	2.01	356.5	182.218	357.87	1.96	0.12	0.23	64.80	355.62	-75.75

Unknown 1	1.48									
Unknown 2	1.35									
Unknown 3	0.9									

Table B.14: GCMS and Thermodynamic Data for Organic compounds in the Aqueous Fraction, recovered Externally for 63.23 % Ash Content Coal

Compound Name	Mass %	Boiling Point (°C)	Molar Mass (g/mol)	Cp (J/molK)	(kJ/kg K)	Flowrate (kg/hr)	mCp (kJ/K)	Hv (kJ/mol)	mHv (kJ/kg)	Heat Evolved (kJ)
2-Propanone. dimethylhydrazone	0.34	87	100.162	110.78	1.11	0.00	0.00	34.90	315.04	-0.56
Acetic acid	3.66	114.1	60.052	110.78	1.84	0.04	0.07	23.70	213.94	-10.08
Propanoic acid	2.36	138.7	74.078	110.78	1.50	0.02	0.04	40.10	361.98	-14.20
Butanoic acid	1.34	161.3	88.105	146.1	1.66	0.01	0.02	42.40	290.21	-7.38
Benzofuran. 2.3-dihydro-	1.01	178.2	120.148	187.41	1.56	0.01	0.02	40.70	217.17	-4.65
Phenol	41.87	181.8	122.164	145.52	1.19	0.44	0.52	43.50	298.93	-205.33
Pentanoic acid	0.7	182.3	102.132	183.75	1.80	0.01	0.01	44.60	242.72	-3.66
Benzofuran. 2.3-dihydro-2-methyl-	0.28	187.4	134.175	229.43	1.71	0.00	0.01	41.60	181.32	-1.25
Phenol. 2-methyl-	34.06	191	108.138	184.27	1.70	0.36	0.61	44.50	241.49	-172.65
Phenol. 2.4-dimethyl-	0.45	210.9	122.164	224.69	1.84	0.00	0.01	46.50	206.95	-2.21
Phenol. 2.3-dimethyl-	7.32	216.9	122.164	224.69	1.84	0.08	0.14	47.20	210.07	-36.18
Phenol. 3.4-dimethyl-	0.68	226.9	122.164	224.69	1.84	0.01	0.01	48.20	214.52	-3.39
Benzoic acid. 3-methyl-	1.69	254.8	136.148	235.84	1.73	0.02	0.03	53.00	224.73	-8.34
Thymine	1.05	366.8	151.4	235.84	1.56	0.01	0.02	68.10	288.76	-5.61
Unknown 1	2.82									

Unknown 2	0.36									

Table B.15: GCMS and Thermodynamic Data for Organic Compounds recovered from Inside the Reactor and Exit tube for 65.75 % Ash Content Coal

Compound Name	Mass %	Boiling Point (°C)	Molar Mass (g/mol)	Cp (J/mol K)	(kJ/kgK)	Flowrate (kg/hr)	mCp (kJ/K)	Hv (kJ/mol)	mHv (kJ/kg)	Heat Evolved (kJ)
p-Xylene /Benzene. 1.3-dimethyl-	1.6	130.6	106.165	211.09	1.99	0.06	0.11	35.70	336.27	-32.96
Cyclohexane. 1-ethyl-4-methyl-. trans- /Cyclohexane. 1-ethyl-4-methyl-. cis-	1.95	143.8	126.239	255.07	2.02	0.07	0.14	37.20	294.68	-39.45
Nonane. 4-methyl-	2.59	159.1	142.28	315.29	2.22	0.09	0.20	38.60	271.30	-55.86
Cyclohexane. (2-methylpropyl)-	6.48	171.3	140.266	299.96	2.14	0.22	0.48	39.10	278.76	-144.51
Decane	4.35	171.9	142.282	315.31	2.22	0.15	0.33	38.80	272.70	-98.30
Phenol	3.99	181.8	94.111	145.52	1.55	0.14	0.21	43.50	462.22	-102.53
Phenol. 2-methyl-	2.97	191	108.138	184.27	1.70	0.10	0.17	44.50	411.51	-75.67
Undecane	2.59	193.3	156.308	360.07	2.30	0.09	0.21	41.50	265.50	-63.64
p-Cresol	6.73	202	108.138	184.27	1.70	0.23	0.40	45.60	421.68	-178.19
Phenol. 2.5-dimethyl-	3.87	211.1	122.164	224.69	1.84	0.13	0.25	46.60	381.45	-102.98
Azulene/Naphthalene	9.94	214.5	128.171	209.58	1.64	0.34	0.56	43.90	342.51	-238.22
Phenol. 2.3-dimethyl-/Phenol. 3.4-dimethyl-	2.18	216.9	122.164	224.69	1.84	0.08	0.14	47.20	386.37	-59.18
Naphthalene. 2-methyl-	6.96	236.9	142.197	252.16	1.77	0.24	0.43	45.70	321.39	-178.41
Tetradecane	1.76	250.9	198.388	505.91	2.55	0.06	0.16	47.10	237.41	-53.37

Naphthalene. 2.6-dimethyl- /Naphthalene. 1.3-dimethyl-	6.1	253.7	156.224	296.31	1.90	0.21	0.40	48.20	308.53	-166.54
1-Naphthalenol	0.89	288	144.06	257.18	1.79	0.03	0.05	54.80	380.40	-27.52
[1.1'-Biphenyl]-4-carboxaldehyde /2.4.6-Cycloheptatrien-1-one. 2-phenyl-	1.75	305.6	182.218	342.32	1.88	0.06	0.11	56.90	312.26	-53.62
9H-Fluorene. 1-methyl-/9H-Fluorene. 2-methyl-	3.22	318	180.245	352.92	1.96	0.11	0.22	53.30	295.71	-102.23
Phenanthrene	3.17	328.4	178.229	334.16	1.87	0.11	0.21	55.80	313.08	-101.79
Anthracene. 2-methyl-	1.57	344.5	192.26	381.22	1.98	0.05	0.11	57.50	299.07	-53.31
9H-Fluoren-9-ol	2.15	356.5	182.218	357.87	1.96	0.07	0.15	64.80	355.62	-78.47
Propane. 1-(1-ethoxyethoxy)-	14.46	130.81	132.2	242.3	1.83	0.50	0.92	35.50	268.53	-254.09
Unknown 1	2.17									
Unknown 2	0.61									
Unknown 3	2.29									
Unknown 4	1.15									-2260.85
Unknown 5	1.76									
Unknown 6	0.72									

Table B.16: GCMS and Thermodynamic Data for Organic Compounds in the of Organic Fraction, recovered Externally for 65.75 % Ash Content Coal

Compound Name	Mass %	Boiling Point (°C)	Molar Mass (g/mol)	Cp (J/molK)	(kJ/kg K)	Flowrate (kg/hr)	mCp (kJ/K)	Hv (kJ/mol)	mHv (kJ/kg)	Heat Evolved (kJ)
o-Xylene	0.2	129.6	106.167	192.5	1.81	0.02	0.04	36.20	340.97	-12.73
Pyridine. 3-methyl-	9.61	140.5	93.13	192.5	2.07	1.06	2.20	37.30	400.52	-733.99
Pyridine. 2.6-dimethyl-	0.42	144	107.153	187.17	1.75	0.05	0.08	37.50	349.97	-27.93
Pyridine. 2-methyl-	0.26	148.4	107.15	187.17	1.75	0.03	0.05	36.20	337.84	-17.16
Pyridine	0.06	148.4	107.15	187.17	1.75	0.01	0.01	35.10	327.58	-3.89
Benzene. 1.2.3-trimethyl-	9.83	156.8	120.192	216.81	1.80	1.09	1.96	39.60	329.47	-665.37
Pyridine. 3.5-dimethyl-	0.23	161.7	107.153	216.81	2.02	0.03	0.05	39.50	368.63	-17.69
Pyridine. 2.3.6-trimethyl-	15.5	177	121.18	216.81	1.79	1.71	3.07	40.00	330.09	-1108.19
Phenol	0.08	181.8	94.111	145.52	1.55	0.01	0.01	43.50	462.22	-6.57
1H-Indene. 1.1-dimethyl-	1.3	186.5	144.213	270.35	1.87	0.14	0.27	42.50	294.70	-92.59
Phenol. 2-methyl-	0.31	191	108.138	184.27	1.70	0.03	0.06	44.50	411.51	-25.26
Phenol. 2.6-dimethyl-	12.37	201.1	122.164	224.69	1.84	1.37	2.52	45.50	372.45	-1015.07
Phenol. 3-ethyl-	4.91	202.7	122.164	224.79	1.84	0.54	1.00	46.60	381.45	-409.48

Phenol. 2-ethyl-4-methyl-	0.94	205.9	136.191	267.07	1.96	0.10	0.20	47.00	345.10	-77.82
Phenol. 2.3.5-trimethyl-	2.48	222.1	136.191	266.77	1.96	0.27	0.54	48.70	357.59	-217.30
Phenol. 3-(1-methylethyl)-	3.31	228	136.19	267.53	1.96	0.37	0.72	48.30	354.65	-293.65
Phenol. 2-(1-methylethyl)-	0.89	228	136.19	267.53	1.96	0.10	0.19	46.80	343.64	-77.87
Naphthalene. 2-methyl-	3.63	236.9	142.197	252.16	1.77	0.40	0.71	45.70	321.39	-297.54
2-Propenal. 3-phenyl-	0.59	237.8	132.16	217.59	1.65	0.07	0.11	48.40	366.22	-49.42
Naphthalene. 1-ethyl-	0.6	239.8	142.197	296.36	2.08	0.07	0.14	47.70	335.45	-55.40
1.1'-Biphenyl. 2-methyl-	1.41	248	168.234	324.5	1.93	0.16	0.30	47.60	282.94	-118.66
Naphthalene. 1.3-dimethyl-	3.99	253.7	156.224	296.31	1.90	0.44	0.84	48.10	307.89	-348.04
Naphthalene. 1.6-dimethyl-	0.54	254.4	156.224	296.31	1.90	0.06	0.11	48.20	308.53	-47.22
Naphthalene. 2.3.6-trimethyl-	0.7	263.5	170.25	342	2.01	0.08	0.16	48.10	282.53	-62.82
Fluorene	0.46	283.6	166.219	306.8	1.85	0.05	0.09	51.20	308.03	-42.28
[1.1'-Biphenyl]-4-carboxaldehyde	0.68	305.6	182.218	342.32	1.88	0.08	0.14	56.90	312.26	-66.63

9H-Fluorene. 2-methyl-	0.24	318	180.245	352.92	1.96	0.03	0.05	53.70	297.93	-24.42
Anthracene	0.46	328.4	178.229	334.16	1.87	0.05	0.10	55.80	313.08	-47.23
Anthracene. 9-methyl-	0.67	347.2	192.26	381.22	1.98	0.07	0.15	56.80	295.43	-72.87
9H-Fluoren-9-ol	0.54	356.5	182.218	357.87	1.96	0.06	0.12	64.80	355.62	-63.02
Unknown 1	16.16									
Unknown 2	2.74									
Unknown 3	2.68									
Unknown 4	0.63									
Unknown 5	0.57									

Table B.17: GCMS and Thermodynamic Data for Organic compounds in the Aqueous Fraction, recovered Externally for 65.75 % Ash Content Coal

Compound Name	Mass %	Boiling Point (°C)	Molar Mass (g/mol)	Cp (J/molK)	(kJ/kg K)	Flowrate (kg/hr)	mCp (kJ/K)	Hv (kJ/mol)	mHv (kJ/kg)	Heat Evolved (kJ)
2-Propanone. dimethylhydrazone	6.17	87	100.162	77.89	0.78	0.12	0.09	34.90	348.44	-8.14
Acetic acid	4.15	114.1	60.052	77.89	1.30	0.08	0.11	23.70	394.66	-11.98
Propanoic acid	4.12	138.7	74.078	110.78	1.50	0.08	0.12	40.10	541.32	-60.18
Phenol. 2.6-dimethyl-	0.49	144	107.153	224.69	2.10	0.01	0.02	45.50	424.63	-6.95
Butanoic acid	1.85	161.3	88.105	146.1	1.66	0.04	0.06	42.40	481.24	-27.02
Benzofuran. 2.3-dihydro-	0.54	178.2	120.148	187.41	1.56	0.01	0.02	40.70	338.75	-6.50
Phenol	37.66	181.8	94.111	145.52	1.55	0.73	1.14	43.50	462.22	-546.09
Pentanoic acid	0.54	182.3	102.132	183.75	1.80	0.01	0.02	44.60	436.69	-8.06
Phenol. 2-methyl-	28.82	191	108.138	184.27	1.70	0.56	0.96	44.50	411.51	-414.34
Phenol. 2.4-dimethyl-	0.89	210.9	122.164	224.69	1.84	0.02	0.03	46.50	380.64	-13.34
Phenol. 2.5-dimethyl-	7.7	211.1	122.164	224.69	1.84	0.15	0.28	46.60	381.45	-115.62
Unknown 1	2.47						0.00			
Unknown 2	2.22									
Unknown 3	0.74									
Unknown 4	0.68									
Unknown 5	0.44									

Unknown 6	0.27									
Unknown 7	0.25									

Appendix C

Sample Calculations

C-1: Pyrolysis and Combustion of Tests at a temperature of 700°C for 30 minutes

The sample calculation was done for a high ash sample (63.23%) as seen in Table A.17.

Ash Content (%)	**63.23**
Mass of Coal Sample before Pyrolysis (g)	11.86
Mass of Coal Sample after Pyrolysis (g)	9.65
Mass Lost from Coal Sample (g)	2.21
Mass of Vial before Pyrolysis (g)	11.34
Mass of Vial after Pyrolysis (g)	12.31
Mass Collected in Vial (g)	0.96
Mass of Reactor + Thermocouple before Pyrolysis (g)	1197.30
Mass of Reactor + Thermocouple after Pyrolysis (g)	1198.50
Mass of Liquid collected in the Reactor (g)	1.20
% Recovery of Volatiles	97.94
% Volatiles (Water + Hydrocarbons)	18.63
Ash Remaining (g)	7.50
% Ash	63.23
% Carbon	18.14

Mass Lost from Coal Sample (g)

$= \text{Mass of Coal Sample before Pyrolysis (g)} - \text{Mass of Coal Sample after Pyrolysis (g)}$

$= 11.86\ \text{g} - 9.65\ \text{g}$

$= 2.21\ \text{g}$

Mass Collected in Vial (g)

$= \text{Mass of Vial after Pyrolysis (g)} - \text{Mass of Vial before Pyrolysis (g)}$

$= 12.31\ \text{g} - 11.34\ \text{g}$

$= 0.96\ \text{g}$

Mass of Liquid collected in the Reactor (g)

$= \text{Mass of Reactor + Thermocouple after Pyrolysis (g)} - \text{Mass of Reactor + Thermocouple (g)}$

$= 1198.50\ \text{g} - 1197.30\ \text{g}$

$= 1.2\ \text{g}$

% **Recovery of Volatiles**

$$= \frac{(\text{Mass of Liquid collected in the Reactor (g)} + \text{Mass Collected in the Vial (g)}}{\text{Mass Lost from Coal Sample (g)}}$$

$$= \frac{(1.2\ \text{g} + 0.96\ \text{g})}{2.21\ \text{g}}$$

$= 97.94\ \%$

% **Volatiles (Water + Hydrocarbons)**

$$= \frac{\text{Mass Lost from Coal Sample (g)}}{\text{Mass of Coal Sample before Pyrolysis (g)}}$$

$$= \frac{2.21\ \text{g}}{11.86\ \text{g}}$$

$= 18.63\ \%$

% **Ash**

$$= \frac{\text{Ash Remaining (g)}}{\text{Mass of Coal Sample before Pyrolysis (g)}}$$

$$= \frac{7.5\ \text{g}}{11.86\ \text{g}}$$

$= 63.23\ \%$

% **Carbon**

$= 100\% - \%\ \text{Volatiles} - \%\ \text{Ash}$

$= 100\ \% - 18.63\ \% - 63.23\ \%$

$= 18.14\%$

Karl Fischer Calculations done for 63.23% sample from Table A.18

Ash Content (%)	Mass of Sample Injected (g)	Water Concentration (ppm)	Percent Water (%)	Average Percent Water (%)	Fraction of Water
63.23	0.0025	79644	7.96	8.12	0.08
	0.0045	83978	8.40		
	0.003	80104	8.01		

For each ash sample the Karl Fischer titration was repeated thrice. The Karl Fischer titration yields water concentration (ppm). The water concentration was converted to (%) and then averaged to give the fraction of water present for the 63.23 % sample as follows:

Convert Water Concentration (ppm) to Percent:

$$\frac{\text{Water Concentration (ppm)}}{1\times10^{-6}}\times100$$

$$= \frac{79644}{1\times10^{-6}} \times 100$$

$$= 7.96$$

Average Percent Water:

$$\frac{7.96 + 8.40 + 8.01}{3} = 8.12\ \%$$

Fraction of Water:

$$\frac{\text{Average Percent Water (\%)}}{100} = 0.08$$

Determining the amount of water present in a 63.23 % sample from Table A.19

Ash Content (%)	**63.23**
Mass Collected in Vial (g)	0.96
0.85	
Top Layer Mass (g) -85%	0.82
Bottom Layer Mass (g) -15%	0.14
Bottom Layer Mass - (Volatiles +Water) - (g)	0.14
2ml of Ethanol (g)	1.58
Bottom Layer Mass - (Volatiles + Water + Solvent)	1.72
Karl Fischer Values	0.08
Mass of Water (g)	0.14
Mass of Volatiles in the Bottom Layer (g)	0.00
Amount of Volatiles (g)	0.82
Amount of Water (g)	0.14
Total Amount of Volatiles (g)	2.02
Total Amount of Water (g)	0.14

The mass of sample collected in the vial was 0.96 g, this sample was centrifuged where the top layer was extracted in hexane. The top layer mass constituted 85%, whilst the bottom layer was 15%. This resulted in a bottom layer mass of 0.14 g. Ethanol (2 mL) was added to the sample which is 1.58 g. This gave a total bottom layer mass of 1.72 g. The Karl Fischer titration yielded 8.12 % of water in the sample which amounted to 0.14 g. Therefore, the amount of volatiles in the bottom layer was 0g. The amount volatiles from the vial was 0.82 g whilst the amount of water was 0.14 g. This yielded a total amount of 2.02 g of volatiles when the mass of volatiles from the tube was added.

Determining the percent of hydrocarbons and water present in a 63.23 % sample.

Ash Content (%)	Mass of Hydrocarbons in Reactor Tube (g)	Mass of Hydrocarbons collected in Vial (g)	Total Mass of Hydrocarbons(g)	Fraction of Hydrocarbons	Percent of Hydrocarbons in Coal Sample	Mass of Water Collected in Vials (g)	Fraction of Water	Percent of Water present in Coal Sample
63,23	1,2	0,82	2,02	0,17	17,07	0,14	0,01	1,18

The total mass of hydrocarbons is the sum of the mass collected in the tube and vial which amounted to 2.02 g. This was divided by the original mass of the coal sample to give 17.07 % of hydrocarbons. Similarly, the percentage of water determined as 1.18 %.

Determining the percent of hydrocarbons and water present in a 63.23 % sample.

Ash Content (%)	Mass of Hydrocarbons in Reactor Tube (g)	Mass of Hydrocarbons collected in Vial (g)	Total Mass of Hydrocarbons(g)	Fraction of Hydrocarbons	Percent of Hydrocarbons in Coal Sample	Mass of Water Collected in Vials (g)	Fraction of Water	Percent of Water present in Coal Sample
63,23	1,2	0,82	2,02	0,17	17,07	0,14	0,01	1,18

The total mass of hydrocarbons is the sum of the mass collected in the tube and vial which amounted to 2.02 g. This was divided by the original mass of the coal sample to give 17.07 % of hydrocarbons. Similarly, the percentage of water determined as 1.18 %.

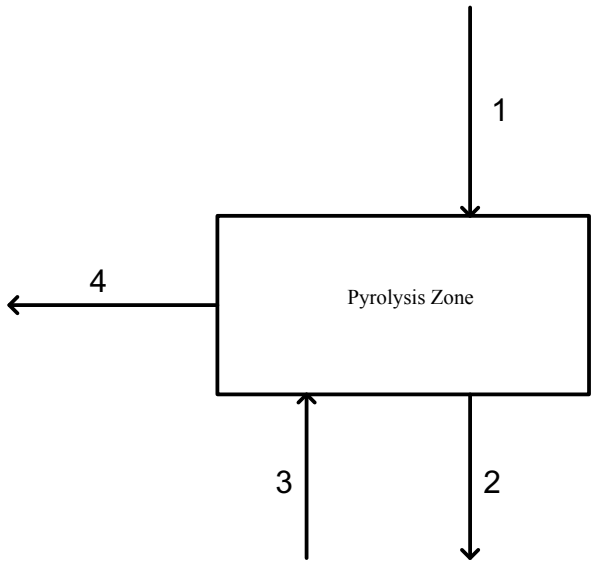
Determining Mass Lost (%) for each temperature range (Adapted from Table A.21)

Ash Content (%)	Temperature (°C)	Time (mins)	Mass Sample (g) + Mass of Crucible	Mass Lost (%)
63.23	26.9°C - 300°C	0	30.5514	0.00
		75	30.5	0.53
	300°C	75	30.5	0.53
		97.5	30.5	0.53
	300°C - 400°C	97.5	30.5	0.53
		142.5	30.5	0.53
	400°C	142.5	30.5	0.53
		165	30.5	0.53
	400°C - 500°C	165	30.5	0.53
		210	30.2	3.64
	500°C	210	30.2	3.64
		232.5	29.5	10.89
	500°C - 600°C	232.5	29.5	10.89
		277.5	29	16.07
	600°C	277.5	29	16.07
		300	28.4	22.29
	600°C - 700°C	300	28.4	22.29
		345	28.4	22.29
	700°C	345	28.4	22.29
		367.5	28.4	22.29

The was of the crucible was 20.9 g. This was subtracted from the total mass of (crucible and sample). Therefore Mass Lost (%) = (1- (Mass Sample/Initial Mass of Sample)) × 100. This was done for every temperature range and used to plot a graph of mass loss vs temperature.

C-2: Sample Calculations for Mass and Energy Balance Circuit – High Ash Sample (63.23 %)

Pyrolysis Zone



<u>Stream 1</u>

Temperature = 25°C

Waterberg Coal Flowrate = 100 kg/hr

Stream Components:

Mass Fraction:

Ash = 0.6323

Hydrocarbons = 0.1743

Water = 0.012

Carbon = 0.1814

Mass Flowrate:

The mass flowrate (kg/hr) was determined using the formula below:

$$\textbf{Mass Flowrate } (\textbf{kg/hr}) = \textbf{ Mass Fraction} \times \textbf{Waterberg Coal Flowrate } (\textbf{kg/hr})$$

Ash (Silica) = 63.23 kg/hr
Volatiles = 17.43 kg/hr
Water = 1.2 kg/hr
Carbon = 18.14 kg/hr

Furthermore, the Volatiles were split into:

Volatiles Mass Fraction:
Inside Components = 0.6
Top Components = 0.34
Bottom Components = 0.06

Volatiles Flowrate = 17.43 kg/hr

Using the above equation, the following flowrates were calculated:

Inside Components = 10.46 kg/hr
Top Components = 5.93 kg/hr
Bottom Components = 1.05 kg/hr

Stream 2

Temperature = 600°C
Mass Flowrate = 81.37 kg/hr

Stream Components:
Ash = 63.23 kg/hr
Carbon = 18.14 kg/hr

Stream 3

Calculated as shown in the combustion zone calculations.

Temperature = ???°C
Mass Flowrate = 173.85 kg/hr

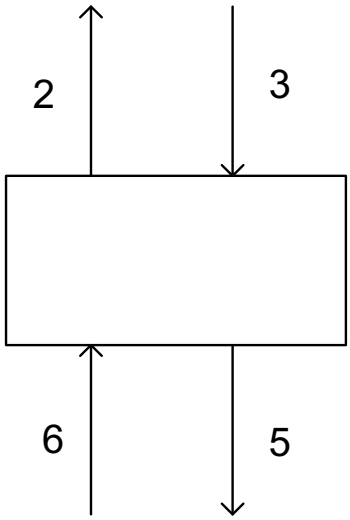
Stream Components:
Nitrogen = 173.85 kg/hr
Carbon dioxide = 33.26 kg/hr
Carbon Monoxide = 21.17 kg/hr

Stream 4

Temperature = 600°C
Mass Flowrate = 192.48 kg/hr

Nitrogen = 119.42 kg/hr
Carbon dioxide = 33.26 kg/hr
Carbon Monoxide = 21.17 kg/hr
Inside Components = 10.46 kg/hr
Top Components = 5.93 kg/hr
Bottom Components = 1.05 kg/hr

Combustion Zone



Stream 2

Temperature = 600°C

Mass Flowrate = 81.37 kg/hr

Stream Components:

Ash = 63.23 kg/hr

Carbon = 18.14 kg/hr

Stream 3

Temperature = 800°C

Mass Flowrate = 173.85 kg/hr

Stream Components:

Nitrogen = 119.42 kg/hr

Carbon dioxide = 33.26 kg/hr

Carbon Monoxide = 21.17 kg/hr

Stream 2

Temperature = 600°C
Mass Flowrate = 63.23 kg/hr

Stream Components:
Ash = 63.23 kg/hr

Stream 6

Temperature = 634.9°C
Mass Flowrate = 173.85 kg/hr

Stream Components:
Nitrogen = 119.42 kg/hr
Oxygen = 36.28 kg/hr

Determining the amount of Nitrogen and Oxygen required:

The amount of carbon entering via Stream 1 was 18.14 kg/hr. The combustion of carbon yields carbon dioxide and carbon monoxide as products. The ratio CO/CO_2 was determined from the Ellingham diagram (Appendix E). The ratio was found to be 1:1 for a combustion zone temperature of 700°C. In this calculation, the combustion zone operating temperature is 800°C. The partial pressure was adjusted to maintain the 1:1 ratio.

The following reactions occur in the combustion zone:

$$C + O_2 \rightarrow CO_2 \quad (1)$$

$$C + \frac{1}{2}O_2 \rightarrow CO \quad (2)$$

Generating a Stoichiometric Table yields the following:

C	O_2	CO_2	CO
1	1	1	
1	0.5		1

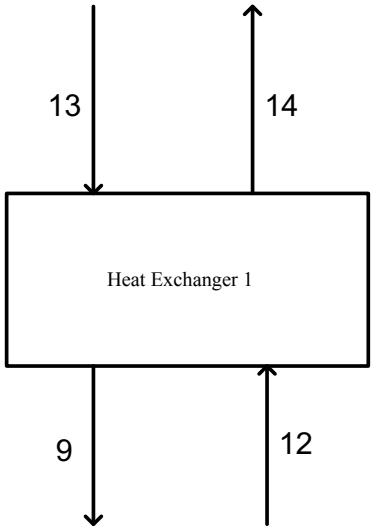
Since the flowrate of carbon is known to be 18.14 kg/hr, the number of moles of carbon was calculated to be 1.51 kmol/hr. The following table was generated:

C	O_2	CO_2	CO
0.76	0.76	0.76	
0.76	0.38		0.76

The composition of air was found to be 21% oxygen (Engineeringtoolbox.com, n.d.), therefore the amount of nitrogen was 79%. The molar mass was obtained from (Felder and Rousseeau, 2000).

No. of Moles (kmol/hr)	No Excess Air	MM	Convert to kg
O_2	1,13	32	36,28
N_2	4,27	28	119,42
C	1,51	12	18,14
CO_2	0,76	44	33,26
CO	0,76	28,01	21,17

Heat Exchanger 1



Cold air enters via Stream 13 and undergoes preheating, starting at heat exchanger 1.

Stream 13

Temperature = 25°C

Mass Flowrate = 155.70 kg/hr

Stream Components:

N_2 = 119.42 kg/hr

O_2 = 36.28 kg/hr

Stream 9

Temperature = ??°C

Mass Flowrate = 155.7 kg/hr

Stream Components:

N_2 = 119.42 kg/hr

O_2 = 36.28 kg/hr

Stream 12

Temperature = 120°C
Mass Flowrate = 175.05 kg/hr

Stream Components:
N_2 = 119.42 kg/hr
H_2O = 1.2 kg/hr
CO = 21.17 kg/hr
CO_2 = 33.26 kg/hr
2-Propanone, dimethylhydrazone = 0.0036 kg/hr
Acetic Acid = 0.04 kg/hr

Stream 14

Temperature = 50°C
Mass Flowrate = 175.05 kg/hr

Stream Components:
N_2 = 119.42 kg/hr
H_2O = 1.2 kg/hr
CO = 21.17 kg/hr
CO_2 = 33.26 kg/hr
2-Propanone, dimethylhydrazone = 0.0036 kg/hr
Acetic Acid = 0.04 kg/hr

The temperature of Stream 9 was calculated using the following equation (Incopera et. al., 2007):

$$Q = mC_p\Delta T$$

Calculating Q for the Hot side:

Firstly, the specific heats were determined:
(Felder and Rousseau, 2000).
For liquid water (Felder and Rousseau, 2000):

$$H_2O\ (l) = \int_{100}^{50} 75.4\times10^{-3}\ dx$$

For the gases: Water, Nitrogen, Carbon Monoxide and Carbon Dioxide the data was obtained from (Liley et. al., 1999):

Name	Molecular Mass (kg/kmol)	C1×1E05	C2×1E05	C3×1E03	C4×1E05	C5
Water	18.015	0.3336	0.2679	2.6105	0.0890	1169
Nitrogen	28.014	0.2911	0.0861	1.7016	0.0010	909.79
Carbon Monoxide	28.010	0.2911	0.0877	3.0851	0.0846	1538.2
Carbon Dioxide	44.010	0.2937	0.3454	1.4280	0.2640	588

Specific Heat = $C1 + C2((C3/T)/sinh(C3/T))^2 + C4((C5/T)/cosh(C5/T))^2$ in J/kmolK

Stream Component	Specific Heat (J/kmol)	Specific Heat (kJ/kg)
N_2	-2043130	-72.93
H_2O (l) – kJ/mol	-3.77	-209.27
H_2O (g)	-682101	-37.86
CO	-2046200	-73.05
CO_2	-2800620	-63.64

The specific heat (J/kmol) was converted by dividing by the molar mass and dividing by 1000 to convert to (kJ/kg).

Also present in Stream 14 were 2-Propanone, dimethylhydrazone and acetic acid. The specific heat was determine using the data found in Appendix B (Table B14).

Substituting the values in the equation:

$$Q_{Hot\ SIde} = \mathrm{mCp\Delta T} = (1.2\times-209.27) + (1.2\times-37.86) + (1.2\times-2.26) + (119.42\times-72.93) + (21.17\times-73.05) + (33.26\times-63.64) + (-1.4) + (-13.13) = -12686.42\ kJ$$

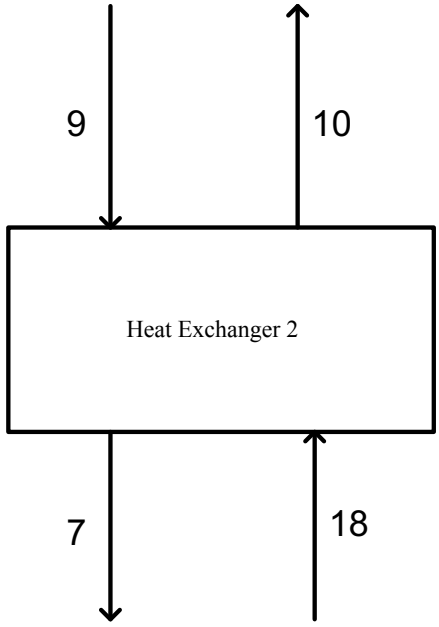
$$\therefore \mathrm{Q_{Cold\ Side}} = 12686.42\ kJ$$

Rearranging: $\mathrm{Q = mCp\Delta T = mCp}(T_2 - T_1)$ to make $\mathrm{T_2}$ the subject of the formula.

$$\therefore \mathrm{T_2} = \frac{\mathrm{Q}}{\mathrm{mCp}} + \mathrm{T_1} = \frac{12686.42}{155.7(1.08)} + 25$$

Substituting the necessary values into the equation and calculating gives $\mathrm{T_9}$ = 100.44°C.

Heat Exchanger 2



Stream 9

Temperature = 100.44 °C

Mass Flowrate = 155.70 kg/hr

Stream Components:

N_2 = 119.42 kg/hr

O_2 = 36.28 kg/hr

Stream 7

Temperature = ??°C

Mass Flowrate = 155.70 kg/hr

Stream Components:

N_2 = 119.42 kg/hr

O_2 = 36.28 kg/hr

Stream 4

Temperature = 600°C

Mass Flowrate = 192.48 kg/hr

Stream Components:

N_2 = 119.42 kg/hr

H_2O = 1.2 kg/hr

CO = 21.17 kg/hr

CO_2 = 33.26 kg/hr

Inside Components = 10.46 kg/hr

Top Components = 5.93 kg/hr

Bottom Components = 1.05 kg.hr

Stream 10

Temperature = ???°C

Mass Flowrate = 192.48 kg/hr

Stream Components:

N_2 = 119.42 kg/hr

H_2O = 1.2 kg/hr

CO = 21.17 kg/hr

CO_2 = 33.26 kg/hr

Inside Components = 10.46 kg/hr

Top Components = 5.93 kg/hr

Bottom Components = 1.05 kg.hr

Since two temperatures were unknown (Stream 4 and Stream 7) the following method was applied to calculate the unknown values:

For the hot side, a value known as Ch was determined as follows:

The hot side has water, nitrogen, carbon dioxide, carbon monoxide, Inside components, Top components and Bottom components.

For the Inside/Top/Bottom Components the GCMS results as shown in Appendix B (Table B.12-B.14) was utilised. The Boiling Point (°C) and Molar Mass (g/mol) were obtained from (Chemspider,2016) whilst the Cp (J/molK) was obtained from Chemeo.

The Cp(J/molK) was converted to Cp (kJ/kg) by dividing by the molar mass. The flowrate was obtained by multiplying the mass percent by total (Inside/Top/Bottom) flowrate. Thereafter a value mCp (kJ/K) was calculated and the values summed for all components. This was done for Tables B.12 – B.14.

For nitrogen, carbon dioxide and carbon monoxide the values were obtained from Engineering Toolbox.

The values obtained are shown in the table below:

Water (g)	2,64
N_2	136,14
CO_2	39,74
CO	24,49
Inside Components	17,21
Top Components	10,47
Bottom Components	1,51

Therefore, Ch =232.21 (kJ/hrK). Similarly, the specific heat of air was obtained and Cc = 168.16 (kJ/hrK)

The minimum C = Cc = 168.16 (kJ.hrK).

$$Q_{max} = C_{min}(T_{h,in} - T_{c,in}) = 168.16(600 - 100.44) = 84004.31\ kJ$$

$$T_{c,out} = T_{c,in} + \left(\frac{Q_{max}}{C_c}\right) = 100.44℃ + \left(\frac{84004.31}{168.16}\right) = 600\,℃$$

$$T_{h,out} = T_{h,in} - \left(\frac{Qmax}{Ch}\right) = 600℃ - \left(\frac{84004.31}{232.21}\right) = 238.24℃$$

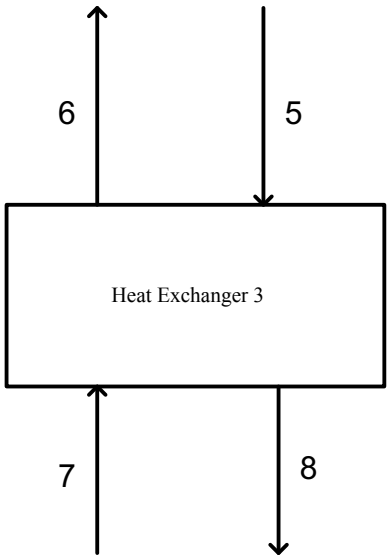
Maintaining a minimum temperature difference of 20°C

$$T_{c,out,new} = 580℃ = T_7$$

$$Q_{new} = Cc(T_{c,out,new} - T_{c,in}) = 168.16(580 - 100.44) = 80641.16kJ$$

$$T_{h,out,new} = T_{h,in} - \left(\frac{Qmax}{Ch}\right) = 580℃ - \left(\frac{80641.16}{232.21}\right) = 252.72℃ = T_4$$

Heat Exchanger 3



Stream 7

Temperature = 580°C

Mass Flowrate = 155.7 kg/hr

Stream Components:

N_2 = 119.42 kg/hr

O_2 = 36.28 kg/hr

Stream 6

Temperature = ??°C

Mass Flowrate = 155.7 kg/hr

Stream Components:

N_2 = 119.42 kg/hr

O_2 = 36.28 kg/hr

Stream 5

Temperature = 800°C

Mass Flowrate = 63.23 kg/hr

Stream Components:

Ash = 63.23 kg/hr

Stream 8

Temperature = 600°C

Mass Flowrate = 63.23 kg/hr

Stream Components:

Ash = 63.23 kg/hr

The temperature of Stream 6 was calculated using the following equation:

$$\mathrm{Q} = \mathrm{mCp}\Delta\mathrm{T}$$

Calculating Q for the Hot side:

Firstly, the heat capacity of Silica was found in literature. The heat was found to be 730 J/kgK.

Substituting the values in the equation:

$$Q_{Hot\ SIde} = \mathrm{mCp}\Delta\mathrm{T} = \frac{63.23 \times 730 \times (600-800)}{1000} = -9231.58\ \mathrm{kJ}$$

$$\therefore \mathrm{Q_{Cold\ Side}} = 9321.58\ kJ$$

Rearranging: $\mathrm{Q} = \mathrm{mCp}\Delta\mathrm{T} = \mathrm{mCp}(T_2 - T_1)$ to make $\mathrm{T_2}$ the subject of the formula.

$$\therefore \mathrm{T_2} = \frac{\mathrm{Q}}{\mathrm{mCp}} + \mathrm{T_1}$$

Substituting the necessary values into the equation and calculating gives $T_9 = 634.89°C$.

Water Cooling

To determine the mass of cooling water required a calculation similar to those done for the heat exchangers was done. Since the hydrocarbons were condensing the Heat of Vaporisation was also accounted for.

Excess energy Sample calculation for 63.23% Ash content

Calculating the heat of reaction at 800°C:

There are 2 reactions that occurred were:

Reaction 1: $C + \frac{1}{2} O_2 \longrightarrow CO$ $\Delta H^o = 110.5$ kJ/mol

Reaction 2: $CO + \frac{1}{2} O_2 \longrightarrow CO_2$ $\Delta H^o = 283$ kJ/mol

Firstly, C_p was calculated using calculations from (Felder and Rousseau, 2000):

CO:

$$\int_{25}^{800} 28.95\times10^{-3} + 0.4110\times10^{-5}\times T + 0.3548\times10^{-8}\times T^2 - 2.220\times10^{-12}\times T^3$$

O_2:

$$\int_{25}^{800} 29.10\times10^{-3} + 1.158\times10^{-5}\times T - 0.6076\times10^{-8}\times T^2 + 1.311\times10^{-12}\times T^3$$

C:

$$\int_{25}^{800} 11.18\times10^{-3} + 1.095\times10^{-5}\times T - 4.891\times10^{10}\times10^{-8}\times T^2$$

Integrate from 298.15K to 1073.15 K to get:

CO: 24.1283 kJ/mol

O_2: 25.3518 kJ/mol

C: 13.2984 kJ/mol

The heat of reaction at 800° = $\Sigma \gamma_i C_p$(products) - $\Sigma \gamma_i C_p$(reactants)

= (1×24.1283) – (0.5×25.3518) – (1×13.2984)

= -1.846 kJ/mol

Therefore, the overall heat of reaction 1 = ΔH^o(25°C) + ΔH_r(800°C)

= 110.5 – 1.846

= 108.654 kJ/mol

Similarly, for reaction 2:

CO: 24.1283 kJ/mol

O_2: 25.3518 kJ/mol

CO_2: 37.3549 kJ/mol

The heat of reaction at 800° = $\Sigma \gamma_i C_p$(products) - $\Sigma \gamma_i C_p$(reactants)

= (1×37.3549) – (0.5×25.3518) – (1×24.1283)

= 0.5507 kJ/mol

Therefore, the overall heat of reaction 2 = $\Delta H^o(25^{\circ}C) + \Delta H_r(800^{\circ}C)$

= 283 + 0.5507

= 283.5507 kJ/mol

Total Energy Released = (1511.67 × 108.65) + (755.83 × 283.55) = 378565 kJ/hr

Energy Required to Heat up the Streams entering the Combustion Zone:

The specific heat was determined to heat up the carbon and ash from 600°C - 800°C, and to heat up the nitrogen and oxygen from 634.89° to 800°C and the follows results were obtained:

C	6443,93
Silica	9231,58
N_2	22982,10
O_2	6515,38
Σ	45172.99

Therefore, the overall energy released = 378656 – 45172.99 = 333392.708 kJ/hr

Appendix D

D-1: Mass and Energy Balance Additional Results

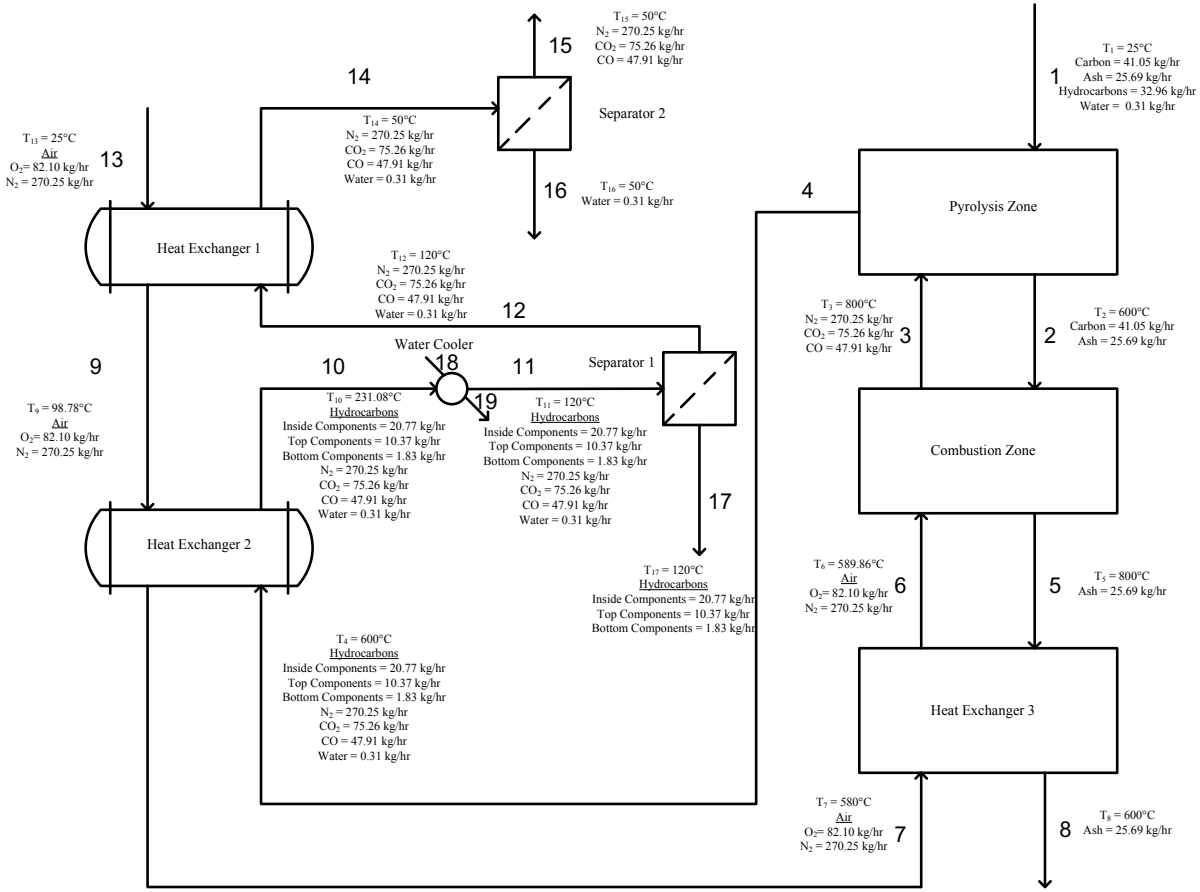


Figure D.1: Mass and Energy Balance Circuit for Low Ash Coal Sample (25.69 %)

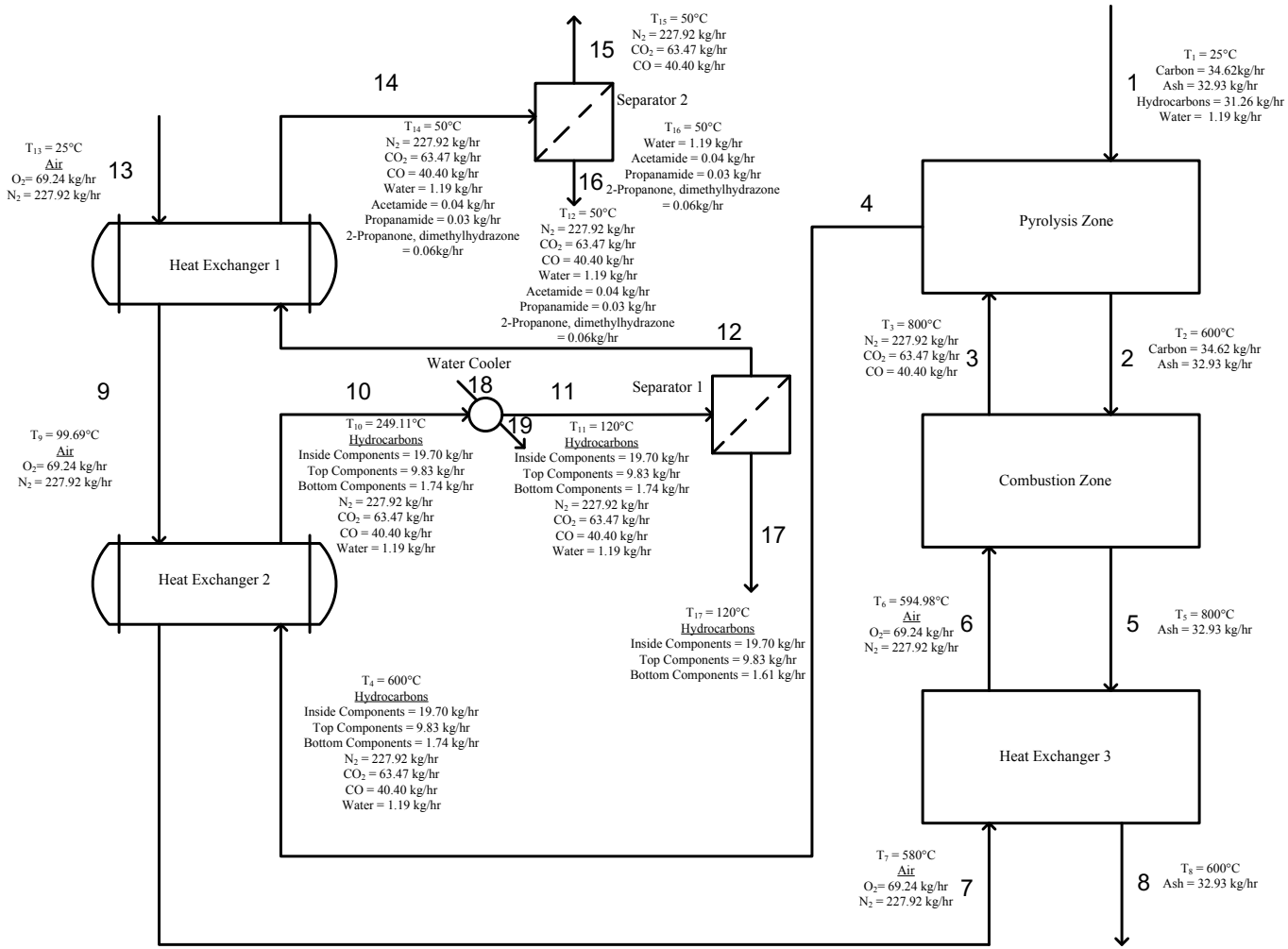


Figure D.2: Mass and Energy Balance Circuit for Low Ash Coal Sample (32.93 %)

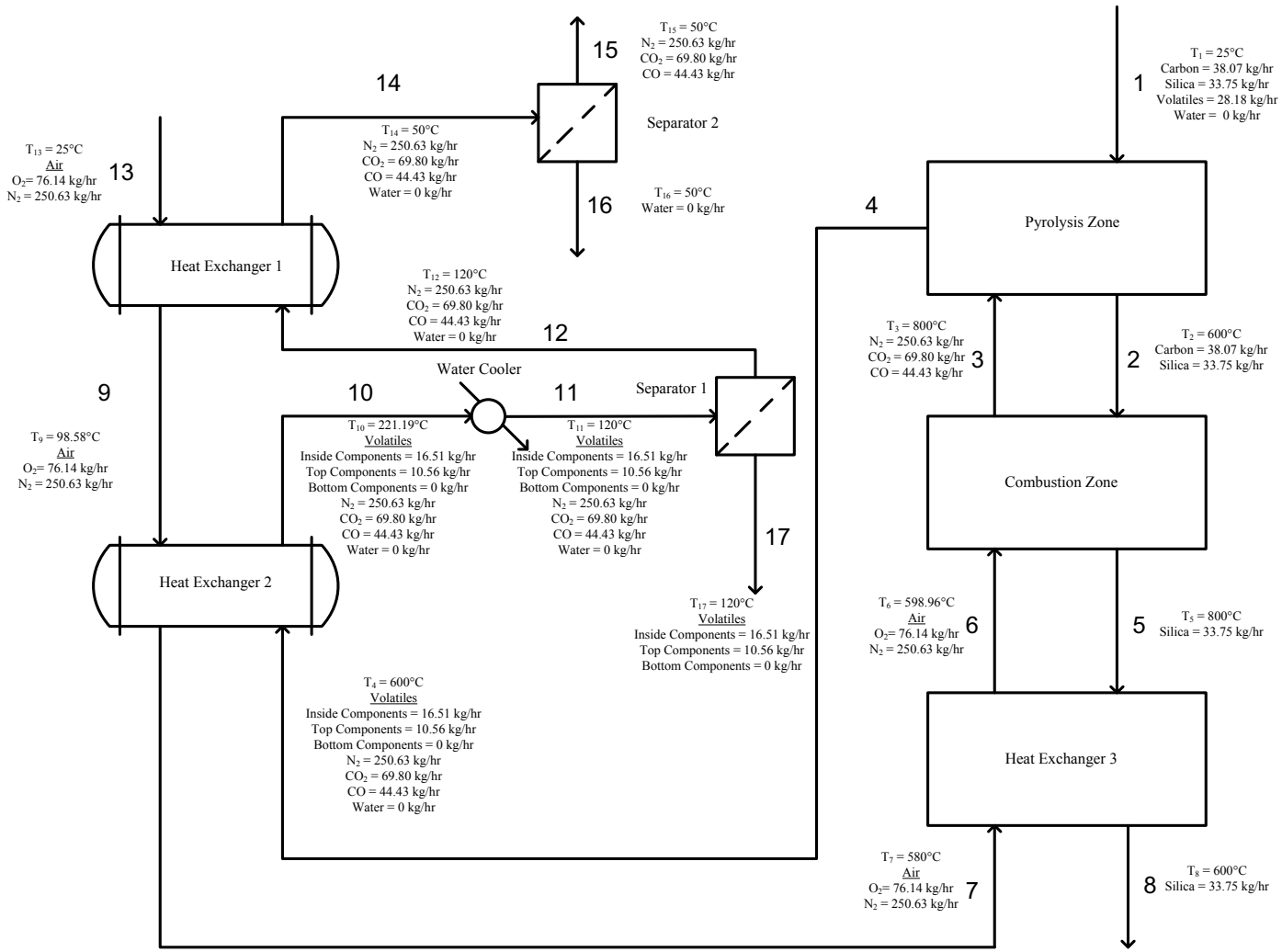


Figure D.3: Mass and Energy Balance Circuit for Low Ash Coal Sample (33.75 %)

Appendix E

E-1: Ellingham Diagram

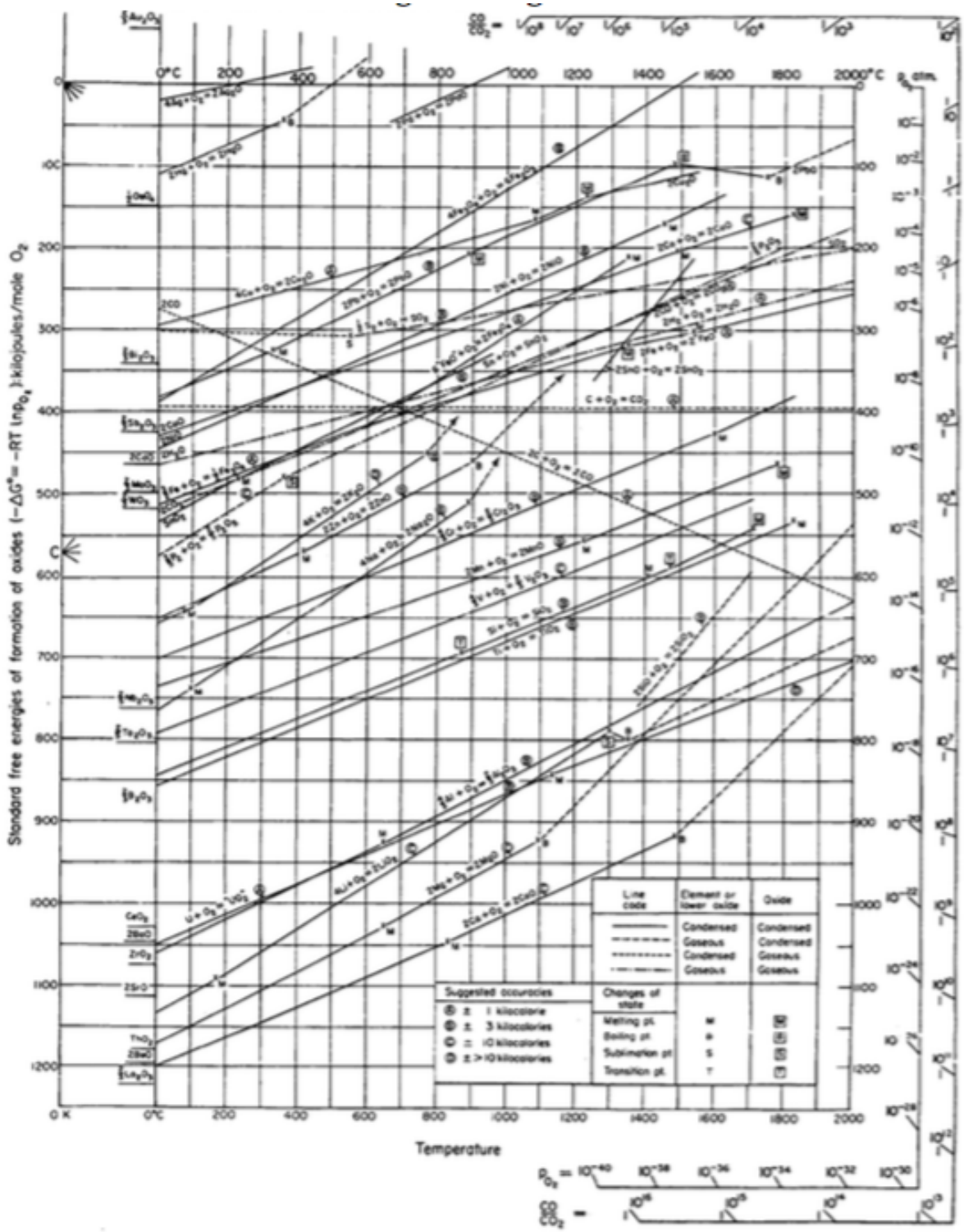


Figure E.1: Ellingham Diagram showing CO/CO_2 ratio for combustion of Carbon (Ellingham Diagrams, n.d)